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° A BRIEF COURSE  
IN  
QUALITATIVE ANALYSIS

BY  
ERNEST A. CONGDON, PH.B., F.C.S.  
*Professor of Chemistry in the Drexel Institute,  
Philadelphia, Pa.*



NEW YORK  
HENRY HOLT AND COMPANY  
1898

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*Professor of Chemistry in the Drexel Institute,  
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## PREFACE.

IT has been the aim in the preparation of this manual to render it as concise as possible with the least sacrifice of a study of reactions and solubilities of chemical importance. For this reason, many of the reactions found in larger books have been omitted.

The following are the points covered in the manual: Preliminary Reactions on Bases and Acids; Schemes of Analysis for Bases and Acids; Brief Explanatory Notes on the Analyses; Treatment of Solid Substances (Powders, Alloys or Metals); Table of Solubilities of salts of the Bases studied. A comprehensive list of questions on Qualitative Analysis, that will force the student *to think*, completes the Manual. These questions, together with the explanatory notes on the schemes of analysis, it is hoped will excite the student's interest and prove a source of inspiration as well as an incentive to intelligent work.

The book is intended merely as a laboratory guide, and should be supplemented by frequent "Quiz Classes" and by constant personal attention. The educational value of such instruction cannot be overestimated.

It is through personal contact with the teacher that the *rationale* of scientific work is understood, and without the requisite amount of this personal instruction Qualitative Analysis becomes mere "test-tubing" and an arbitrary and perfunctory thing, instead of the branch of logical Science which it is.

This Brief Course has been satisfactorily given in the Drexel Institute within the allotted time of one laboratory

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period (four hours) and one hour for a lecture or quiz per week, during the school year of thirty-two weeks.

I take pleasure in acknowledging the advice and assistance received from Mr. Abraham Henwood, Instructor in Chemistry in the Drexel Institute, in the preparation of this manual.

E. A. C.

PHILADELPHIA, PA.,

May 1, 1898.





# LABORATORY INSTRUCTIONS.

## Qualitative Analysis.

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### Classification of the Metals for Use in Chemical Analysis.

#### GROUP I.

Silver, lead, mercury (*mercurous*).

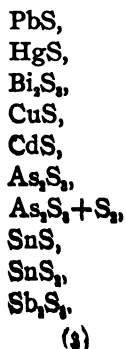
Precipitated by the group reagent, hydrochloric acid, HCl,  
as:—



#### GROUP II.

Lead (imperfectly removed by reagent of Group I.), mercury (*mercuric*), bismuth, copper, cadmium, arsenic (*arsenious* and *arsenic*), tin (*stannous* and *stannic*), antimony.

Precipitated by the group reagent, hydrogen sulphide, H<sub>2</sub>S, as:—



**GROUP III.**

Iron (*ferrous* and *ferric*), aluminium, chromium, nickel, cobalt, manganese, zinc.

Precipitated by the group reagent, ammonium sulphide,  $(\text{NH}_4)_2\text{S}$ , as:—

$\text{FeS}$  (from both *ferrous* and *ferric* compounds),  
 $\text{Al}(\text{OH})_3$ ,  
 $\text{Cr}(\text{OH})_3$ ,  
 $\text{NiS}$ ,  
 $\text{CoS}$ ,  
 $\text{MnS}$ ,  
 $\text{ZnS}$ .

**GROUP IV.**

Barium, strontium, and calcium.

Precipitated by the group reagent, ammonium oxalate, as:—

$\text{BaC}_2\text{O}_4$ ,  
 $\text{SrC}_2\text{O}_4$ ,  
 $\text{CaC}_2\text{O}_4$ .

**GROUP V.**

Magnesium, potassium, sodium (ammonium).

Not precipitated by a group reagent.







## A.—Reactions of the Metals.

### GROUP I.

SILVER. Ag.

Valence = I.

Use preferably  $\text{AgNO}_3$ .

1.  $\text{HCl}$  precipitates  $\text{AgCl}$ .

White, curdy, darkens on exposure to light.

Soluble in  $\text{NH}_4\text{OH}$ ,  $\text{KCN}$ .

Insoluble in  $\text{HNO}_3$  and other dilute mineral acids; soluble in concentrated  $\text{HCl}$ .

2.  $\text{H}_2\text{S}$  or alkaline sulphides precipitate  $\text{Ag}_2\text{S}$ .

Black.

Insoluble in alkaline sulphides.

Insoluble in dilute mineral acids.

Soluble in boiling  $\text{HNO}_3$ .

3.  $\text{NH}_4\text{OH}$ ,  $\text{NaOH}$ , or  $\text{KOH}$  precipitates  $\text{Ag}_2\text{O}$ .

Brown.

Insoluble in excess of  $\text{NaOH}$  or  $\text{KOH}$ ; soluble in excess of  $\text{NH}_4\text{OH}$ .

Soluble in  $\text{HNO}_3$ .

4.  $\text{KCN}$  precipitates  $\text{AgCN}$ .

White, curdy.

Soluble in excess of  $\text{KCN}$ .

Soluble in  $\text{NH}_4\text{OH}$ .

Insoluble in  $\text{HNO}_3$ .

5. Heated with the blowpipe on charcoal, +  $\text{Na}_2\text{CO}_3$ , silver is reduced from all its compounds and forms bright malleable globules which are soluble in  $\text{HNO}_3$ .

LEAD. Pb.

Valence = II.

Use preferably  $\text{Pb}(\text{NO}_3)_2$ .

6.  $\text{HCl}$  precipitates  $\text{PbCl}_2$ .

White, pulverulent.

Insoluble in alcohol.

Decidedly soluble in cold water.

Completely soluble in boiling water.

Soluble in sodium acetate and salts of organic acids.

Soluble in concentrated HCl.

7.  $H_2S$  or alkaline sulphides precipitate  $PbS$ .

Black. (All lead compounds are blackened by  $H_2S$ .)

Insoluble in excess of alkaline sulphides.

Insoluble in quite dilute mineral acids.

Soluble in hot, moderately concentrated  $HNO_3$ .

Converted to  $PbSO_4$  by concentrated  $HNO_3$ .

8.  $NH_4OH$ ,  $NaOH$ , or  $KOH$  precipitates  $Pb(OH)_2$ .

White.

Insoluble in excess of  $NH_4OH$ .

Soluble in excess of  $NaOH$  and  $KOH$ .

9.  $KCN$  precipitates  $Pb(CN)_2$ .

White, pulverulent.

Insoluble in excess of  $KCN$ .

Soluble in  $HNO_3$ .

10.  $H_2SO_4$  precipitates  $PbSO_4$ .

White, pulverulent.

Insoluble in dilute mineral acids.

Insoluble in alcohol.

Soluble in excess of concentrated  $H_2SO_4$ .

Soluble in alkaline solutions of salts of organic acids, especially acetic and tartaric.

11.  $K_2CrO_4$  or  $K_2Cr_2O_7$  precipitates  $PbCrO_4$ .

Yellow.

Soluble in  $HNO_3$  with difficulty.

Soluble in  $NaOH$  or  $KOH$ .

12. Heated with the blowpipe on charcoal, +  $Na_2CO_3$ , lead is reduced from all its compounds and forms soft, malleable, easily fusible globules which yield a yellow incrustation of  $PbO$ .





MERCURY (*Mercurous*). Hg. Valence = I.

Use preferably  $\text{Hg}_2(\text{NO}_3)_2$ .

13.  $\text{HCl}$  precipitates  $\text{Hg}_2\text{Cl}_2$ .

White, pulverulent.

Converted by  $\text{NH}_4\text{OH}$  into  $\text{NH}_2\text{Hg}_2\text{Cl}$ , black.

Oxidizing agents convert  $\text{Hg}_2\text{Cl}_2$  into the soluble chloride,  $\text{HgCl}_2$ .

14.  $\text{NH}_4\text{OH}$  precipitates  $\text{NH}_2\text{Hg}_2\text{NO}_3$ .

Black.

15.  $\text{NaOH}$  or  $\text{KOH}$  precipitates  $\text{Hg}_2\text{O}$ .

Black. (Readily decomposes into  $\text{HgO} + \text{Hg}$ .)

16.  $\text{SnCl}_2$  precipitates  $\text{Hg}_2\text{Cl}_2$  and finally metallic Hg, grey.

17. Heated in a glass tube with dry  $\text{Na}_2\text{CO}_3$ , mercury is reduced from all its compounds. It is vaporized and condenses in the cooler part of the tube, forming globules.



### Scheme of Analysis of Group I.

+ dilute HCl.		
Ppt = AgCl.	PbCl <sub>2</sub> .	Hg <sub>2</sub> Cl <sub>2</sub> .
Treat + hot water.		
Residue = AgCl, Hg <sub>2</sub> Cl <sub>2</sub> . Treat + NH <sub>4</sub> OH.		Solution PbCl <sub>2</sub> . Confirm Pb by 7, 10 or 11.
Residue NH <sub>4</sub> Hg <sub>2</sub> Cl.	Solution NH <sub>4</sub> AgCl.	
Confirm Hg by 17.	Confirm Ag by 1.	

### Alternative Scheme.

+ HCl, dilute. Filter and treat precipitate.

+ KOH in excess.	
Residue = AgCl. Hg <sub>2</sub> Cl <sub>2</sub> or Hg <sub>2</sub> O.	Solution K <sub>2</sub> PbO <sub>3</sub> . Confirm Pb by 7.
Mix + dry Na <sub>2</sub> CO <sub>3</sub> . Heat in glass tube to completely expel Hg. Forms mirror. Collect globules of Hg. Dissolve in HNO <sub>3</sub> . Confirm Hg by 21. Residue Ag <sub>2</sub> O, NaCl, excess Na <sub>2</sub> CO <sub>3</sub> . Treat with hot water. Dissolve residue in dilute HNO <sub>3</sub> . Confirm by 1.	

*Note.*—Examine filtrate from precipitation + HCl, for remaining groups.





### Notes on Analysis of Group I.

I. Lead is not completely removed in the first group by the reagent HCl, as the  $PbCl_2$  dissolves somewhat in water; hence small amounts of Pb are always found in Group II. if the metal has been found in Group I.

II. The action of  $NH_4OH$  after the removal of the Pb is to convert the  $AgCl$  and  $Hg_2Cl_2$  into substituted ammonium compounds. The first of these, being soluble, is found in the filtrate, and the second, an insoluble compound, remains as a black residue.

III. Compounds of metals of the first group are reduced with particular ease when heated on charcoal with  $Na_2CO_3$ , giving metallic globules all of which are easily soluble in  $HNO_3$ . (For mercury a glass tube closed at one end is used.)

IV. Note that silver compounds are, as a rule, soluble in  $NH_4OH$  but not in NaOH or KOH; lead compounds are insoluble in  $NH_4OH$  but easily soluble in NaOH or KOH; and mercurous compounds are insoluble in both.

### GROUP II.

MERCURY (*Mercuric*). Hg. Valence = II.

Use preferably  $HgCl_2$ .

18.  $H_2S$  or alkaline sulphides precipitate finally  $HgS$ .  
Black.

Insoluble in  $HNO_3$ .

Insoluble in  $(NH_4)_2S$ .

Soluble in  $Na_2S$ ,  $K_2S$ .

Soluble in NaOH, KOH.

Soluble in aqua regia ( $HCl + HNO_3$ ) or in other mixtures yielding Cl.

19.  $\text{NH}_4\text{OH}$  precipitates  $\text{NH}_2\text{HgCl}$ .  
White (distinction from *Mercurous*, see 14).
20.  $\text{KOH}$  or  $\text{NaOH}$  precipitates finally  $\text{HgO}$ .  
Yellow.  
Insoluble in excess of reagent.
21.  $\text{SnCl}_2$  precipitates  $\text{Hg}_2\text{Cl}_2$  and finally metallic  $\text{Hg}$ .  
White at first and finally grey.
22. See 17.

BISMUTH. Bi. Valence = III.

Use preferably  $\text{BiCl}_3$ .

23.  $\text{H}_2\text{S}$  or alkaline sulphides precipitate  $\text{Bi}_2\text{S}_3$ .  
Very dark brown.  
Insoluble in dilute acids.  
Insoluble in alkaline hydroxides.  
Insoluble in alkaline sulphides.  
Insoluble in  $\text{KCN}$ .  
Soluble in moderately concentrated  $\text{HNO}_3$ .
24.  $\text{NH}_4\text{OH}$ ,  $\text{NaOH}$ ,  $\text{KOH}$  precipitates  $\text{Bi}(\text{OH})_3$ .  
White, flocculent.  
Insoluble in excess of reagent.
25.  $\text{H}_2\text{O}$  precipitates  $\text{BiOCl}$ .  
White, pulverulent.  
Insoluble in tartaric acid (distinction from antimony).
26.  $\text{K}_2\text{SnO}_3$  in excess, precipitates  $\text{Bi}_2\text{O}_3$ .  
Black.

COPPER. Cu. Valence = II.

Use preferably  $\text{CuSO}_4$ .

27.  $\text{H}_2\text{S}$  or soluble sulphides precipitate  $\text{CuS}$ .  
Brownish black.  
Insoluble in  $\text{Na}_2\text{S}$  and  $\text{K}_2\text{S}$ .  
Insoluble in  $\text{KOH}$  or  $\text{NaOH}$ .







Insoluble in dilute acids.

Soluble in  $\text{HNO}_3$ .

Very slightly soluble in  $(\text{NH}_4)_2\text{S}$ .

Soluble in KCN.

Oxidized, when moist, to  $\text{CuSO}_4$  by O in the air.

28.  $\text{NH}_4\text{OH}$  precipitates  $\text{Cu}(\text{OH})_2$ , immediately soluble in excess forming a deep blue solution.
29.  $\text{KOH}$  or  $\text{NaOH}$  precipitates  $\text{Cu}(\text{OH})_2$ .  
Light blue.  
Insoluble in excess of reagent.  
Converted by boiling into  $\text{CuO}$ , black.
30.  $\text{K}_4\text{Fe}(\text{CN})_6$  precipitates  $\text{Cu}_2\text{Fe}(\text{CN})_6$ , reddish brown.  
This forms even in very dilute solutions.
31.  $\text{Fe}$  or  $\text{Zn}$ , in neutral or acid solutions, precipitates metallic  $\text{Cu}$ .
32. Heated with the blowpipe on charcoal +  $\text{Na}_2\text{CO}_3$ , copper is reduced from all its compounds and forms red malleable grains.
33. Copper compounds color beads of borax or microcosmic salt, blue in the oxidizing flame and opaque red (due to  $\text{Cu}_2\text{O}$ ) in the reducing flame.
34. Copper compounds acidified with  $\text{HCl}$  color the flame blue or green.

CADMIUM.  $\text{Cd}$ .

Valence = II.

Use preferably  $\text{CdSO}_4$ .

35.  $\text{H}_2\text{S}$  or alkaline sulphides precipitate  $\text{CdS}$ .  
Yellow.  
Insoluble in dilute  $\text{HCl}$ .  
Insoluble in alkaline sulphides.  
Insoluble in  $\text{NaOH}$  and  $\text{KOH}$ .  
Insoluble in KCN.  
Soluble in  $\text{HNO}_3$ , and in boiling  $\text{H}_2\text{SO}_4$  and  $\text{HCl}$ .

36.  $\text{NH}_4\text{OH}$  precipitates  $\text{Cd}(\text{OH})_2$ .  
White.  
Soluble in excess of reagent.
37.  $\text{NaOH}$  or  $\text{KOH}$  precipitates  $\text{Cd}(\text{OH})_2$ .  
White.  
Insoluble in excess of reagent.
38. All compounds of  $\text{Cd}$  when heated on charcoal with  $\text{Na}_2\text{CO}_3$ , give  $\text{CdO}$  as a brown tarnish which exhibits a play of colors.

ARSENIC (*Arsenious*).  $\text{As}$ . Valence = III.

Use preferably  $\text{Na}_3\text{AsO}_3$ .

39.  $\text{H}_2\text{S}$  precipitates from acid solutions,  $\text{As}_2\text{S}_3$ .  
Yellow.  
Insoluble in concentrated  $\text{HCl}$ .  
Soluble in concentrated  $\text{HNO}_3$ .  
Soluble in alkaline sulphides.  
Soluble in alkaline carbonates and hydroxides.
40.  $\text{AgNO}_3$  added to neutral solutions precipitates  $\text{Ag}_3\text{AsO}_3$ .  
Yellow. (Easily soluble in  $\text{HNO}_3$  and in  $\text{NH}_4\text{OH}$ .)
41. Nascent hydrogen acting on arsenic solutions produces in all cases  $\text{AsH}_3$  gas (*highly poisonous!*) "Marsh Test." Inflammable—burns to  $\text{As}_2\text{O}_3 + \text{H}_2\text{O}$ .  
Arsenic, as a lustrous mirror, is separated if the flame be chilled, *e. g.* by the introduction of cold porcelain.  
Dissociated by heat with the separation of metallic  $\text{As}$ . Soluble in  $\text{HNO}_3$ ; in  $\text{NaClO}$ .  
Passed into a solution of  $\text{AgNO}_3$  forms  $\text{H}_3\text{AsO}_3$ . Neutralized + dilute  $\text{NH}_4\text{OH}$  forms  $\text{Ag}_3\text{AsO}_3$ . Yellow ring.
42. A strip of copper added to solutions of arsenic compounds acidified with  $\text{HCl}$ , and heated, becomes





coated with a gray deposit. (Reinsch Test.) On heating this strip in an open tube with free access of air, the white oxide  $\text{As}_2\text{O}_3$  is formed. Crystalline and easily volatilized.

43. All arsenic compounds heated on charcoal +  $\text{Na}_2\text{CO}_3$  are reduced to arsenic which volatilizes with a characteristic garlic-like odor.
44. Oxidizing agents, such as  $\text{HNO}_3$ ,  $\text{Cl}$ ,  $\text{NaClO}$ ,  $\text{K}_2\text{Cr}_2\text{O}_7$ ,  $\text{K}_2\text{Mn}_2\text{O}_8$ , convert *arsenious* into *arsenic* compounds.

ARSENIC (*Arsenic*). As. Valence = V.

Use preferably  $\text{Na}_3\text{AsO}_4$ .

45.  $\text{H}_2\text{S}$  reduces *arsenic* compounds to *arsenious* with the separation of S. It then precipitates  $\text{As}_2\text{S}_3$ .  
Yellow.  
See 39.
46. Alkaline sulphides precipitate  $\text{As}_2\text{S}_3$ .  
Yellow.  
Insoluble in  $\text{HCl}$ .  
Soluble in excess of reagents.
47.  $\text{MgSO}_4$  in the presence of  $\text{NH}_4\text{Cl}$  +  $\text{NH}_4\text{OH}$  precipitates  $\text{MgNH}_4\text{AsO}_4$ .  
White, crystalline.  
Insoluble in  $\text{NH}_4\text{OH}$ .  
Easily soluble in dilute acids.
48. See 41.
49. See 42.
50. See 43.
51. Reducing agents, such as  $\text{H}_2\text{S}$ ,  $\text{SO}_2$ , convert *arsenic* into *arsenious* compounds.

TIN (Stannous). Sn. Valence = II.

Use preferably  $\text{SnCl}_2$ .

52.  $\text{H}_2\text{S}$  precipitates  $\text{SnS}$ .  
Brown.  
Insoluble in alkaline mono-sulphides.  
Insoluble in dilute acids.  
Soluble in alkaline poly-sulphides.  
Soluble in alkaline hydroxides.  
Soluble in concentrated  $\text{HCl}$ .
53. Alkaline sulphides precipitate  $\text{SnS}$ .  
Brown.  
Soluble in excess of the reagent, if poly-sulphides are used.
54. Alkaline hydroxides precipitate  $\text{Sn(OH)}_2$ .  
White.  
Insoluble in excess of  $\text{NH}_4\text{OH}$ .  
Soluble in excess of  $\text{NaOH}$  and  $\text{KOH}$ .
55.  $\text{HgCl}_2$  is reduced by stannous salts with the precipitation of  $\text{Hg}_2\text{Cl}_2$ ; later  $\text{Hg}$  precipitates.  
(See 21. Distinction from stannic compounds.)
56. All tin compounds, when mixed with  $\text{Na}_2\text{CO}_3$  and  $\text{KCN}$  and heated on charcoal, are reduced to globules of  $\text{Sn}$ , with an accompanying white incrustation of  $\text{SnO}_2$ .  
Moistened with  $\text{Co(NO}_3)_2$  and heated with blowpipe, a bluish green color results.
57. Oxidizing agents, such as  $\text{HNO}_3$ ,  $\text{Cl}$ ,  $\text{Fe}_2\text{Cl}_6$ , convert stannous compounds to stannic.

TIN (Stannic). Sn. Valence = IV.

Use preferably  $\text{SnCl}_4$ .

58.  $\text{H}_2\text{S}$  precipitates  $\text{SnS}_2$ .  
Yellow.  
Insoluble in dilute acids.







Insoluble in  $(\text{NH}_4)_2\text{CO}_3$ .  
 Soluble in concentrated  $\text{HCl}$ .  
 Soluble in alkaline sulphides.  
 Soluble in fixed alkaline hydroxides.

59. Alkaline sulphides precipitate  $\text{SnS}_2$ .  
 Yellow.  
 Soluble in excess of the reagent.
60. Alkaline hydroxides precipitate  $\text{SnO}(\text{OH})_2$ .  
 White.  
 Insoluble in excess of  $\text{NH}_4\text{OH}$ .  
 Soluble in excess of  $\text{KOH}$  and  $\text{NaOH}$ .
61. Neutral salts of the alkali metals, such as  $\text{Na}_2\text{SO}_4$  and  $\text{NH}_4\text{NO}_3$ , give on boiling a precipitate of stannic or meta-stannic acid,  $\text{H}_2\text{SnO}_3$ , or  $(\text{H}_2\text{SnO}_3)_n$ .
62. See 56.
63. Reducing agents, such as nascent hydrogen and certain metals ( $\text{Sn}$ ,  $\text{Cu}$ ), convert stannic compounds first to stannous and finally, in some cases, to metallic  $\text{Sn}$ .

ANTIMONY.  $\text{Sb}$ . Valence = III.

Use preferably  $\text{SbCl}_3$ .

64.  $\text{H}_2\text{S}$  precipitates  $\text{Sb}_2\text{S}_3$ .  
 Orange-red.  
 Insoluble in dilute acids.  
 Insoluble in  $(\text{NH}_4)_2\text{CO}_3$ .  
 Soluble in alkaline sulphides.  
 Soluble in alkaline hydroxides.  
 Soluble in concentrated  $\text{HCl}$ .  
 Soluble in hot concentrated  $\text{H}_2\text{C}_4\text{H}_4\text{O}_6$ .
65. Alkaline sulphides precipitate  $\text{Sb}_2\text{S}_3$ .  
 Orange-red.  
 Soluble in excess of the reagent.

66. Alkaline hydroxides precipitate  $\text{Sb}(\text{OH})_3$ .  
 White.  
 Insoluble in excess of  $\text{NH}_4\text{OH}$ .  
 Soluble in excess of  $\text{KOH}$  and  $\text{NaOH}$ .
67.  $\text{H}_2\text{O}$  causes the precipitation of  $\text{SbOCl}$ .  
 White.  
 Easily soluble in  $\text{H}_2\text{C}_4\text{H}_4\text{O}_6$ . (Distinction from  $\text{Bi}$ .)
68. Analogous to arsenic. See 41. The gas  $\text{SbH}_3$ , passed into a solution of  $\text{AgNO}_3$ , precipitates  $\text{Ag}_3\text{Sb}$ . (Distinction from  $\text{As}$ .)  
 Metallic  $\text{Sb}$  is converted into  $\text{Sb}_2\text{O}_3$  by means of  $\text{HNO}_3$ ; insoluble in  $\text{NaClO}$ . (Distinctions from  $\text{As}$ .)
69. Zinc in the presence of  $\text{HCl}$  and  $\text{Pt}$  precipitates  $\text{Sb}$  as a dull black adherent coating on the  $\text{Pt}$ . Insoluble in  $\text{HCl}$ . Converted into oxide by  $\text{HNO}_3$ .
70. Heated with  $\text{Na}_2\text{CO}_3$  on charcoal in the reducing flame, brittle beads of  $\text{Sb}$  are formed. These are easily converted by oxidation into the volatile  $\text{Sb}_2\text{O}_3$ , which coats the coal. Moistened with  $\text{Co}(\text{NO}_3)_2$ , and ignited, an olive green color is developed.





## Scheme of Analysis of Group II.

+  $\text{H}_2\text{S}$  gas through warm, dilute solution, acid with  $\text{HCl}$ .

Precipitate:

( $\text{PbS}$ ),  $\text{HgS}$ ,  $\text{Bi}_2\text{S}_3$ ,  $\text{CuS}$ ,  $\text{CdS}$ ,  $\text{SnS}$ ,  $\text{SnS}_2$ ,  $\text{As}_2\text{S}_3$ ,  $\text{Sb}_2\text{S}_3$ .

(Filtrate to be examined for remaining groups.)

Digest +  $(\text{NH}_4)_2\text{S}_x$  warm.

<p><b>Residue:</b> (<math>\text{PbS}</math>) <math>\text{HgS}</math>, <math>\text{Bi}_2\text{S}_3</math>, <math>\text{CuS}</math>, <math>\text{CdS}</math>. Treat + hot dilute <math>\text{HNO}_3</math> (1-1).</p>	<p><b>Filtrate.</b> <math>(\text{NH}_4)_2\text{AsS}_5</math>, <math>(\text{NH}_4)_3\text{SbS}_6</math>, <math>(\text{NH}_4)_2\text{SnS}_5</math> + dilute <math>\text{H}_2\text{SO}_4</math>.</p>
<p><b>Residue:</b> (<math>\text{PbSO}_4</math>) <math>\text{HgS}</math>, <math>\text{S}</math>. Boil + aqua regia. <b>Solution—</b> <math>\text{HgCl}_2</math>. Confirm <math>\text{Hg}</math> by 21.</p>	<p><b>Precipitate:</b> <math>\text{SnS}_2</math>, <math>\text{Sb}_2\text{S}_3</math>, <math>\text{As}_2\text{S}_3</math>. + concentrated <math>\text{HCl}</math> and boil.</p>
<p><b>Precip.:</b> <math>\text{PbSO}_4</math>. Confirm <math>\text{Pb}</math> by 7.</p>	<p><b>Residue:</b> <math>\text{As}_2\text{S}_3</math>. Dissolve in <math>\text{HNO}_3</math>. Confirm <math>\text{As}</math> by 47.</p>
<p>+ <math>\text{NH}_4\text{OH}</math> in excess.</p>	<p><b>Solution:</b> <math>\text{SnCl}_4</math>, <math>\text{SbCl}_5</math>. Dilute + <math>\text{H}_2\text{O}</math>. Add <math>\text{Zn}</math> + <math>\text{Pt}</math>. <math>\text{Sb}</math> precipitated on <math>\text{Pt}</math>. Confirm <math>\text{Sb}</math> by 69. <math>\text{Sn}</math> precipitated on <math>\text{Zn}</math>. Confirm <math>\text{Sn}</math> after solution in <math>\text{HCl}</math> by 55.</p>
<p><b>Precip.:</b> <math>\text{Bi}(\text{OH})_3</math>. Confirm <math>\text{Bi}</math> by 26.</p>	<p><b>Filtrate:</b> <math>\text{NH}_4</math> salts of <math>\text{Cu}</math> + <math>\text{Cd}</math>. Deep blue if <math>\text{Cu}</math> is present. Acidify + <math>\text{HCl}</math>. + Clean Iron.</p>
<p><b>Precip.:</b> <math>\text{Cu}</math>. <math>\text{Red}</math>.</p>	<p><b>Solution:</b> Dilute + <math>\text{H}_2\text{O}</math>. pass <math>\text{H}_2\text{S}</math> — = <math>\text{CdS}</math> — yellow. Confirm <math>\text{Cd}</math> by 38.</p>

## Alternative Scheme of Analysis.

+ H<sub>2</sub>S through warm, dilute solution, acid + HCl.

Precipitate:

(PbS), HgS, Bi<sub>2</sub>S<sub>3</sub>, CuS, CdS, As<sub>2</sub>S<sub>3</sub>, Sb<sub>2</sub>S<sub>3</sub>, SnS, SnS<sub>2</sub>.

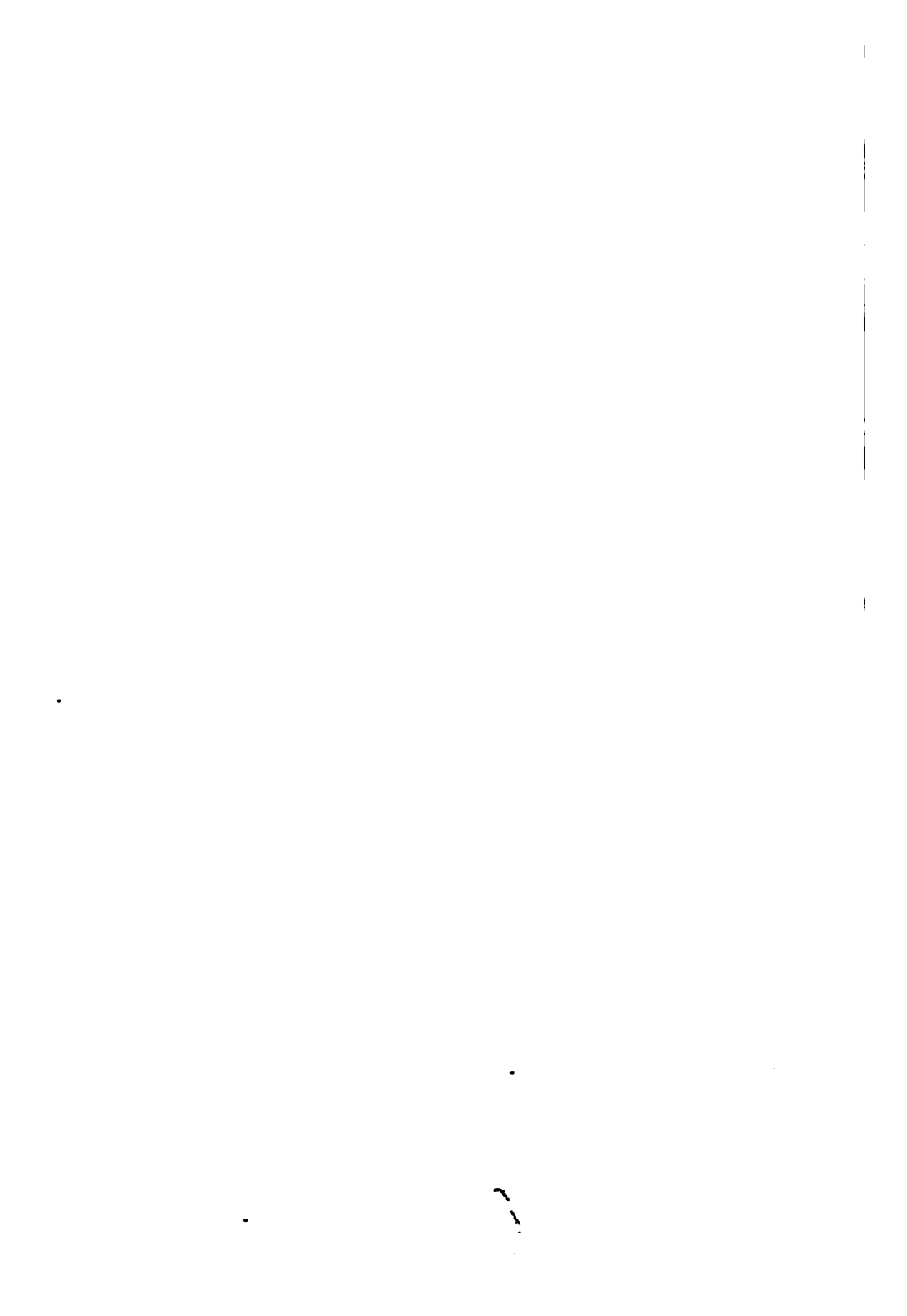
(Filtrate to be examined for remaining groups.)

Digest + (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub> warm.

Residue: (PbS), HgS, Bi <sub>2</sub> S <sub>3</sub> , CuS, CdS. Treat + dilute HNO <sub>3</sub> (1-1).	Filtrate: Pb(NO <sub>3</sub> ) <sub>2</sub> , Bi(NO <sub>3</sub> ) <sub>3</sub> , Cu(NO <sub>3</sub> ) <sub>2</sub> , Cd(NO <sub>3</sub> ) <sub>2</sub> .	
	+ dilute H <sub>2</sub> SO <sub>4</sub> .	
Residue: PbSO <sub>4</sub> ), HgS, S. Examine as in first scheme given for Group II.	Precipitate PbSO <sub>4</sub> :	
	Filtrate: Bi(NO <sub>3</sub> ) <sub>3</sub> , Cu(NO <sub>3</sub> ) <sub>2</sub> , Cd(NO <sub>3</sub> ) <sub>2</sub> . Boil out excess HNO <sub>3</sub> , dilute, neutralize + NaOH, and add excess KCN.	
Precipitate:		Solution:
Bi(OH) <sub>3</sub> , Confirm Bi by 26.		Cu(CN) <sub>2</sub> , 2KCN. Cd(CN) <sub>2</sub> , 2KCN. Pass H <sub>2</sub> S.
Precip.:		Solution:
CdS. Yellow.		Cu(CN) <sub>2</sub> , 2KCN. + NaClO X S. — Blue Solution. Boil — CuO and CuS. Black.

Filtrate: (NH <sub>4</sub> ) <sub>2</sub> As <sub>2</sub> S <sub>3</sub> , (NH <sub>4</sub> ) <sub>2</sub> Sb <sub>2</sub> S <sub>3</sub> , (NH <sub>4</sub> ) <sub>2</sub> SnS <sub>2</sub> , + dilute H <sub>2</sub> SO <sub>4</sub> . As <sub>2</sub> S <sub>3</sub> , SnS <sub>2</sub> , Sb <sub>2</sub> S <sub>3</sub> . Boil + excess saturated solution H <sub>2</sub> C <sub>2</sub> O <sub>4</sub> .	Residue:	Filtrate:
	As <sub>2</sub> S <sub>3</sub> , Sb <sub>2</sub> S <sub>3</sub> . Dissolve in HCl + KClO <sub>4</sub> . Boil to expel excess Cl. Introduce solution into H gas generating flask. Pass gases evolved through solution AgNO <sub>3</sub> .	Sn(C <sub>2</sub> O <sub>4</sub> ) <sub>2</sub> . Evaporate + H <sub>2</sub> SO <sub>4</sub> until fumes of SO <sub>3</sub> appear. Allow to become cold. Dilute + H <sub>2</sub> O. Pass H <sub>2</sub> S. Precipitate SnS <sub>2</sub> . Yellow.
Precipitate:		Filtrate: H <sub>2</sub> AsO <sub>3</sub>
AgSb + HCl. Filter. Residue, AgCl. Reject.		Neutralize + dilute NH <sub>4</sub> OH. Yellow precipitate — Ag <sub>2</sub> AsO <sub>3</sub> See 41.
Solution: SbCl <sub>3</sub> Confirm by 64 or 67.		







## Notes on Analysis of Group II.

I. At the time of the precipitation of the second group by  $\text{H}_2\text{S}$ ,  $\text{HNO}_3$  and other oxidizing agents should be absent, or present only in very small amounts. On boiling the solution down to a small bulk with  $\text{HCl}$ , these oxidizing agents are eliminated;  $\text{HNO}_3$ , chlorine or chlorine oxides being volatilized, whereas chromates and permanganates are reduced.

The presence of oxidizing agents is objectionable because they oxidize the  $\text{H}_2\text{S}$ , forming  $\text{H}_2\text{O}$ ,  $\text{S}$ , or even  $\text{H}_2\text{SO}_4$ ; they also have a solvent effect on the sulphides formed, and so prevent a complete precipitation.

The best conditions for the precipitation of Group II. by  $\text{H}_2\text{S}$  are:—

Dilute solution.

Slightly acid +  $\text{HCl}$ .

Moderately warm.

II. Sulphides of the members of the second group are somewhat soluble in mineral acids unless the acids are quite dilute.  $\text{CdS}$ ,  $\text{Sb}_2\text{S}_3$ , and  $\text{SnS}_2$  dissolve quite easily in  $\text{HCl}$ .  $\text{HgS}$  is insoluble in  $\text{HNO}_3$  (concentrated  $\text{HNO}_3$  may convert  $\text{HgS}$  on boiling to white basic compounds).  $\text{PbS}$  dissolves easily in  $\text{HNO}_3$ —a portion of it, however, being converted into white insoluble  $\text{PbSO}_4$ . Boiling saturated solution of oxalic acid dissolves  $\text{SnS}_2$ , but does not affect  $\text{As}_2\text{S}_3$  or  $\text{Sb}_2\text{S}_3$ .  $(\text{NH}_4)_2\text{S}_x$  dissolves easily  $\text{SnS}$ ,  $\text{SnS}_2$ ,  $\text{As}_2\text{S}_3$ ,  $\text{Sb}_2\text{S}_3$ , and small amounts of  $\text{CuS}$ .  $(\text{NH}_4)_2\text{S}$ , colorless, dissolves these last named, with the exception of  $\text{SnS}$ .  $\text{Na}_2\text{S}$  or  $\text{K}_2\text{S}$  dissolves  $\text{SnS}_2$ ,  $\text{Sb}_2\text{S}_3$ ,  $\text{As}_2\text{S}_3$ , and appreciable amounts of  $\text{HgS}$ .  $\text{CuS}$ ,  $\text{CdS}$ ,  $\text{Bi}_2\text{S}_3$  are insoluble in fixed alkaline sulphides.

Moist copper sulphide is easily oxidized by the oxygen of the air, forming  $\text{CuSO}_4$ ; hence the sulphides of the second group should not be allowed to stand.

All sulphides are dissolved by oxidizing agents. (Exception:  $\text{HNO}_3$  converts  $\text{Sb}_2\text{S}_3$  and  $\text{SnS}_2$  into the corresponding oxides, and does not dissolve  $\text{HgS}$ .)

III.  $\text{NH}_4\text{OH}$  dissolves hydroxides of Cu and Cd. KOH or NaOH dissolves hydroxides of Pb, Sn, and Sb. Neither  $\text{NH}_4\text{OH}$  nor KOH nor NaOH dissolves compounds of Hg and Bi.

(Arsenic compounds are not precipitated by alkaline hydroxides.)

IV. KCN precipitates solutions of Pb, Bi, Cu, and Cd. Bismuth precipitates as hydroxide with the evolution of HCN. The cyanides of Cu and Cd dissolve in excess, forming  $\text{Cu}(\text{CN})_{3/2}$  KCN,  $\text{Cd}(\text{CN})_{3/2}$  KCN.

V. Cupric salts, when treated with  $\text{NH}_4\text{CNS}$  and saturated with  $\text{SO}_2$ , give a precipitate of  $\text{Cu}_2(\text{CNS})_2$ . White. This distinguishes Cu from all metals but those of the first group.

VI. Compounds of metals of the second group are easily reduced to the metallic state when heated on charcoal with  $\text{Na}_2\text{CO}_3$ . Tin compounds require the addition of KCN. Bismuth easily oxidizes, yielding a yellow coat on the coal. Cadmium forms a coat on the coal which has a characteristic iridescence. Tin forms a white oxide that deposits near the reduced metal. This oxide, on being moistened with  $\text{Co}(\text{NO}_3)_2$ , gives a blue-green mass. Antimony easily oxidizes, forming a volatile white coat that collects on the coal for some distance from the reduced metal. This oxide, on being moistened with  $\text{Co}(\text{NO}_3)_2$ , and heated with the blow-pipe, gives an olive green mass. Arsenic compounds, on being reduced on the coal, give off a characteristic garlic-like odor. Copper compounds give no coat on the coal. For behavior of mercury compounds, see Note III. on Group I., and No. 17.

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### GROUP III.

IRON (*Ferrous*). Fe. Valence = II.

Use preferably  $\text{FeSO}_4$ .

71.  $(\text{NH}_4)_2\text{S}$  and fixed alkaline sulphides precipitate FeS.





Black.

Insoluble in excess of reagent.

Soluble in dilute mineral acids.

Oxidized by the air to  $\text{FeSO}_4$  and basic ferric compounds.

72. Alkaline hydroxides precipitate  $\text{Fe}(\text{OH})_2$ . White, immediately changing to dirty green and finally to reddish brown. Due to oxidation.

Insoluble in excess of  $\text{NaOH}$  or  $\text{KOH}$ .

Soluble in  $\text{NH}_4\text{OH}$  in the presence of ammonium salts, the solution precipitating on exposure to air, due to formation of ferric compounds.

73.  $\text{K}_3\text{Fe}(\text{CN})_6$  precipitates  $\text{Fe}_3\text{Fe}_2(\text{CN})_{12}$ .  
Blue. (Distinction from ferric.)

74. All compounds of iron fused in a bead of borax, give in the reducing flame a pale green bead, and in the oxidizing flame one which is brown or yellow when hot, often colorless when cold.

75. Oxidizing agents, such as  $\text{HNO}_3$ ,  $\text{Cl}$ ,  $\text{Br}$ ,  $\text{KClO}_3$ ,  $\text{K}_2\text{Mn}_2\text{O}_8$ ,  $\text{K}_2\text{Cr}_2\text{O}_7$ , convert *ferrous* into *ferric* compounds.

FERRIC.  $\text{Fe}$ . Valence = III.

Use preferably  $\text{Fe}_2\text{Cl}_6$ .

76.  $(\text{NH}_4)_2\text{S}$  and fixed alkaline sulphides precipitate  $\text{FeS} + \text{S}$ . See 71.
77. Alkaline hydroxides precipitate  $\text{Fe}_2(\text{OH})_6$ .  
Reddish-brown.  
Insoluble in excess of reagent.  
Precipitation prevented by presence of organic substances, such as tartaric acid, citric acid, and sugar.
78.  $\text{BaCO}_3$  suspended in water precipitates  $\text{Fe}_2(\text{OH})_6$ , with the evolution of  $\text{CO}_2$  gas. (Distinction from *ferrous* compounds.)

All soluble carbonates precipitate  $\text{Fe}_2(\text{OH})_6$  with evolutions of  $\text{CO}_2$ .

79.  $\text{KCNS}$  or  $\text{NH}_4\text{CNS}$  produces  $\text{Fe}_2(\text{CNS})_6$ .  
 Blood-red solution.  
 Not destroyed by  $\text{HCl}$ .
80.  $\text{NaC}_2\text{H}_3\text{O}_2$  in neutral solutions or those slightly acid with  $\text{HC}_2\text{H}_3\text{O}_2$  produces  $\text{Fe}_2(\text{C}_2\text{H}_3\text{O}_2)_6$ , which is deep red. On being boiled, reddish brown basic ferric acetates are precipitated.
81. See 74.
82. Reducing agents, such as  $\text{H}_2\text{S}$ ,  $\text{SO}_2$  and nascent hydrogen, convert ferric into ferrous compounds.

#### ALUMINIUM. Al. Valence = III.

Use preferably  $\text{Al}_2(\text{SO}_4)_3$ .

83.  $(\text{NH}_4)_2\text{S}$  and fixed alkaline sulphides precipitate  $\text{Al}_2(\text{OH})_6$  with the evolution of  $\text{H}_2\text{S}$  gas.  
 White, flocculent.  
 Insoluble in excess of reagent.
84. Alkaline hydroxides precipitate  $\text{Al}_2(\text{OH})_6$ .  
 White, flocculent.  
 Slightly soluble in excess of  $\text{NH}_4\text{OH}$  (rendered less soluble by the presence of ammonium salts).  
 Easily soluble in excess of  $\text{NaOH}$  and  $\text{KOH}$ ; hot or cold.
85.  $\text{BaCO}_3$  suspended in water precipitates  $\text{Al}_2(\text{OH})_6$  with the evolution of  $\text{CO}_2$ .
86. Heated with blowpipe on charcoal, aluminium compounds yield, when moistened with  $\text{Co}(\text{NO}_3)_2$ , and again ignited, a sky-blue infusible mass.
87.  $\text{Na}(\text{C}_2\text{H}_3\text{O}_2)$  analogous to ferric iron. See 80.







## CHROMIUM. Cr. Valence = III.

Use preferably  $\text{Cr}_2(\text{SO}_4)_3$ .

88.  $(\text{NH}_4)_2\text{S}$  or fixed alkaline sulphides precipitate  $\text{Cr}_2(\text{OH})_6$ .  
Grayish green.  
Insoluble in excess of reagents.  
Insoluble in hot  $\text{NaOH}$  or  $\text{KOH}$ .  
Soluble in excess of cold alkaline hydroxides. Reprecipitated by prolonged boiling. Slightly soluble in large excess of  $\text{NH}_4\text{OH}$ .
89. Alkaline hydroxides precipitate  $\text{Cr}_2(\text{OH})_6$ . See 88.
90.  $\text{BaCO}_3$  suspended in water precipitates  $\text{Cr}_2(\text{OH})_6$ , with the evolution of  $\text{CO}_2$ .
91.  $\text{NaC}_2\text{H}_3\text{O}_2$  analogous to ferric iron. See 80.
92. Chromium compounds, heated on a loop of Pt wire with borax or microcosmic salt, dissolve, giving a clear emerald green bead.
93. Oxidizing agents, such as  $\text{Cl}$ ,  $\text{Br}$ ,  $\text{NaClO}$ , convert solutions of chromium salts to yellow alkaline chromates. Solid chromium compounds, fused with  $\text{Na}_2\text{CO}_3$  and  $\text{KNO}_3$  or  $\text{KClO}_3$ , yield alkaline chromates, yellow, soluble in water.

## NICKEL. Ni. Valence = II.

Use preferably  $\text{Ni}(\text{NO}_3)_2$ .

94.  $(\text{NH}_4)_2\text{S}$  or fixed alkaline sulphides precipitate  $\text{NiS}$ .  
Black.  
Insoluble in cold dilute  $\text{HCl}$  (1—6).  
Insoluble in acetic acid.  
Slightly soluble in excess of  $(\text{NH}_4)_2\text{S}_x$ , particularly in the presence of  $\text{NH}_4\text{OH}$ , giving inky brown solution. Distinction from  $\text{Co}$ . (The presence of ammonium salts hinders this solubility.)  
Easily soluble in aqua regia.

95.  $\text{NH}_4\text{OH}$  precipitates  $\text{Ni}(\text{OH})_2$ , immediately soluble in excess, particularly in presence of ammonium salts, giving a blue solution.
96.  $\text{NaOH}$  or  $\text{KOH}$  precipitates  $\text{Ni}(\text{OH})_2$ .  
 Light green.  
 Insoluble in excess of reagent.  
 Soluble in ammonium salts.
97.  $\text{KCN}$  precipitates  $\text{Ni}(\text{CN})_2$ .  
 Yellowish green.  
 Insoluble in dilute  $\text{HCl}$ .  
 Soluble in excess of reagent.  
 This solution + excess  $\text{NaOH}$  or  $\text{KOH}$ , and treated with oxidizing agents such as  $\text{Cl}$  or  $\text{Br}$  or  $\text{HgO}$ , gives a precipitate of  $\text{Ni}_2(\text{OH})_6$ , black. (Distinction from  $\text{Co}$ .)
98. All nickel compounds dissolve completely in borax and microcosmic salt beads, imparting to them in the oxidizing flame a brownish color; in the reducing, a gray. (This color is obscured by the presence of  $\text{Co}$  compounds.)

COBALT.  $\text{Co}$ .

Valence = II.

Use preferably  $\text{Co}(\text{NO}_3)_2$ .

99.  $(\text{NH}_4)_2\text{S}$  or fixed alkaline sulphides precipitate  $\text{CoS}$ .  
 Insoluble in cold dilute  $\text{HCl}$  (1-6).  
 Insoluble in acetic acid.  
 Insoluble in excess of reagent.  
 Easily soluble in aqua regia.
100.  $\text{NH}_4\text{OH}$  precipitates  $\text{Co}(\text{OH})_2$ , immediately soluble in excess, giving a reddish-brown solution.
101.  $\text{NaOH}$  or  $\text{KOH}$  precipitates blue basic salts.  
 Converted by boiling into  $\text{Co}(\text{OH})_2$ .  
 Pink.  
 Insoluble in excess of reagents.





102. KCN precipitates  $\text{Co}(\text{CN})_2$ .  
Brownish-white.  
Insoluble in dilute HCl.  
Soluble in excess of reagent. This solution on prolonged boiling with a few drops of HCl is oxidized by the oxygen of the air to the soluble  $\text{K}_3\text{Co}(\text{CN})_6$ .  
(Distinction from Ni.)
103.  $\text{KNO}_3$  in solutions, acid only with acetic acid, precipitates  $\text{K}_3\text{Co}(\text{NO}_2)_6$ .  
Yellow, crystalline.  
Insoluble in acetic acid.  
Soluble in HCl.
104. Cobalt compounds dissolve completely in borax and microcosmic salt beads, giving an intensely deep blue color, appearing black when large amounts of cobalt are present.

MANGANESE.    Mn.                  Valence = II.

Use preferably  $\text{MnSO}_4$ .

105.  $(\text{NH}_4)_2\text{S}$  or fixed alkaline sulphides precipitate  $\text{MnS}$ .  
Flesh-tint.  
Insoluble in excess of reagents.  
Easily soluble in dilute mineral acids and in acetic acid  
(this latter a distinction from  $\text{ZnS}$ ).
106.  $\text{NH}_4\text{OH}$  precipitates  $\text{Mn}(\text{OH})_2$ .  
White.  
Insoluble in excess of reagent.  
Soluble in ammonium salts, hence precipitation does not take place in their presence. But on standing this solution becomes turbid and  $\text{Mn}_2\text{O}_3(\text{OH})_2$ , brown, separates because of atmospheric oxidation.
107.  $\text{NaOH}$  or  $\text{KOH}$  precipitates  $\text{Mn}(\text{OH})_2$ .  
White, turning brown on exposure to air.  
Insoluble in excess of reagents.

108. Manganese compounds, fused in a bead of microcosmic salt or borax, impart in the oxidizing flame an amethyst red color, which becomes colorless in the reducing flame.

If the hot microcosmic salt bead is laid on a crystal of  $\text{KNO}_3$  or  $\text{NaNO}_3$ , an intense violet coloration is developed.

109. Oxidizing agents, such as  $\text{HNO}_3 + \text{PbO}_2$  or  $\text{Pb}_2\text{O}_3$ , Cl or Br in alkaline solutions, convert solutions of manganous salts into permanganic acid or soluble permanganates, purple.

Solid compounds fused on Pt with  $\text{Na}_2\text{CO}_3 + \text{KNO}_3$  or  $\text{KClO}_3$ , form manganates, deep blue-green. Boiled with water these dissolve, forming purple permanganates and insoluble  $\text{MnO}_2$ .

Bromine precipitates from acetic acid solutions,  $\text{MnO}_2$ , brown.

ZINC. Zn.

Valence = II.

Use preferably  $\text{ZnSO}_4$ .

110.  $(\text{NH}_4)_2\text{S}$  or fixed alkaline sulphides precipitate  $\text{ZnS}$ .  
White.

Insoluble in excess of reagents.

Insoluble in acetic acid.

(Distinction from  $\text{MnS}$ .)

Easily soluble in dilute min. acids.

111.  $\text{NH}_4\text{OH}$  or fixed alkaline hydroxides precipitate  $\text{Zn}(\text{OH})_2$ .

White.

Readily soluble in excess of reagents.

112. Heated on charcoal with  $\text{Na}_2\text{CO}_3$ ,  $\text{ZnO}$  is produced, yellow while hot, white when cold; moistened with  $\text{Co}(\text{NO}_3)_2$ , and heated again, it gives a green infusible mass.







### Analysis of Group III.

+  $\text{NH}_4\text{OH}$  in slight excess. Warm, and allow precipitate to settle.  
 Precipitate =  $\text{FeS}$ ,  $\text{Al}_2(\text{OH})_6$ ,  $\text{Cr}_2(\text{OH})_6$ ,  $\text{CoS}$ ,  $\text{NiS}$ ,  $\text{ZnS}$ ,  $\text{MnS}$ .  
 (Filtrate to be examined for following groups.)  
 Precipitate + cold dilute  $\text{HCl}$  (1-6).

<b>Residue:</b> NiS, CoS. Dissolve in aqua regia. Boil to dryness. Dissolve in water. + excess KCN, then NaClO. Digest with HgO.	<b>Precipitate:</b> Ni <sub>2</sub> (OH) <sub>6</sub> . Black. Confirm by 98.	<b>Filtrate:</b> =K <sub>2</sub> Co(CN) <sub>6</sub> . +H <sub>2</sub> SO <sub>4</sub> . Evaporate to dryness. Confirm by 104.
	<b>Residue:</b> Fe <sub>2</sub> (OH) <sub>6</sub> , Mn <sub>2</sub> O <sub>3</sub> (OH) <sub>2</sub> . Dissolve + HCl and boil out Cl. Allow to cool. Neutralize with Na <sub>2</sub> CO <sub>3</sub> . Add NaC <sub>2</sub> H <sub>3</sub> O <sub>2</sub> . Boil.	<b>Filtrate:</b> Al <sub>2</sub> (ONa) <sub>6</sub> , Na <sub>2</sub> CrO <sub>4</sub> , Zn(ONa) <sub>2</sub> . +NH <sub>4</sub> Cl in excess, and warm.
	<b>Precipitate:</b> Al <sub>2</sub> (OH) <sub>6</sub> . White. Gelatinous. Confirm by 86.	<b>Filtrate:</b> +HC <sub>2</sub> H <sub>3</sub> O <sub>2</sub> in excess. +H <sub>2</sub> S gas to saturation.
	<b>Precipitate:</b> Basic Ferric acetate. Brown. Flocculent. Dissolve in HCl, and confirm by 79.	<b>Filtrate:</b> +NaOH till alkaline, then(NH <sub>4</sub> ) <sub>2</sub> S. MnS. Flesh tint. Confirm by 108.
	<b>Precipitate:</b> ZnS, white. Confirm by 112.	<b>Filtrate:</b> Cr <sub>2</sub> (C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> ) <sub>6</sub> . +NH <sub>4</sub> OH Cr <sub>2</sub> (OH) <sub>6</sub> . Green. Flocculent. Confirm by 92.

### Alternative Analysis of Group III.

+  $\text{NH}_4\text{OH}$  in slight excess. Warm, and allow precipitate to settle.  
 +  $(\text{NH}_4)_2\text{S}$  in slight excess. Precipitate =  $\text{FeS}$ ,  $\text{Al}(\text{OH})_3$ ,  $\text{Cr}(\text{OH})_3$ ,  $\text{CoS}$ ,  $\text{NiS}$ ,  $\text{ZnS}$ ,  $\text{MnS}$ .  
 (Filtrate to be examined for following groups.)  
 + Aqua regia and boil out chlorine and excess of acid.  
 $\text{Fe}_2\text{Cl}_6$ ,  $\text{Al}_2\text{Cl}_6$ ,  $\text{Cr}_2\text{Cl}_6$ ,  $\text{CoCl}_2$ ,  $\text{NiCl}_2$ ,  $\text{ZnCl}_2$ ,  $\text{MnCl}_2$   
 +  $\text{BaCO}_3$  suspended in water. Shake well in flask. Allow to stand.

Precipitate: $\text{Fe}(\text{OH})_3$ , $\text{Cr}(\text{OH})_3$ , $\text{Al}(\text{OH})_3$ Excess $\text{BaCO}_3$ Boil + excess $\text{KOH}$ .		Filtrate: $\text{NiCl}_2$ , $\text{CoCl}_2$ , $\text{ZnCl}_2$ , $\text{MnCl}_2$ ( $\text{BaCl}_2$ ). Add a large quantity of acetic acid. + $\text{H}_2\text{S}$ through cold mod. dilute solution.	
Residue:	Filtrate:	Precip.:	Filtrate:
$\text{Fe}(\text{OH})_3$ , $\text{Cr}(\text{OH})_3$ , Fuse + $\text{KNO}_3$ and $\text{Na}_2\text{CO}_3$ . Extract + $\text{H}_2\text{O}$ . Residue: $\text{Fe}_2\text{O}_3$ + $\text{HCl}$ . Confirm by 79.	$\text{Al}_3(\text{ONa})_6$ , + $\text{NH}_4\text{Cl}$ . Boil —. $\text{Al}_3(\text{OH})_6$ . Confirm by 86.	$\text{Co}(\text{C}_2\text{H}_3\text{O}_2)_2$ , $(\text{NiC}_2\text{H}_3\text{O}_2)_2$ , $\text{Mn}(\text{C}_2\text{H}_3\text{O}_2)_2$ . Nearly neutralize with $\text{Na}_2\text{CO}_3$ . Warm solution. Pass $\text{H}_2\text{S}$ .	Precipitate: $\text{NiS}$ , $\text{CoS}$ . Dissolve in aqua regia. Boil out $\text{Cl}$ . Make alkaline + $\text{KOH}$ . Filter. Dissolve precipitate in $\text{HCl}$ , $\text{H}_2\text{O}_2$ + $\text{KNO}_3$ . Allow to stand.
	Filtrate: $\text{K}_2\text{CrO}_4$ , $\text{Na}_2\text{CrO}_4$ . Confirm $\text{Cr}$ by 11.	Precipitate: $\text{Mn}(\text{C}_2\text{H}_3\text{O}_2)_2$ + $\text{KOH}$ . $\text{MnS}$ , $\text{Mn}(\text{OH})_2$ . Confirm by bead. See 108.	Precipitate: $\text{K}_2\text{Co}(\text{NO}_2)_6$ . Confirm by bead. See 104.
			Filtrate: + $\text{KOH}$ = $\text{Ni}(\text{OH})_2$ . Confirm by bead. See 98.

See 104. Community Fund.  
See 104.



**Scheme for Analysis of Third Group in Presence of  
(a) Oxalic Acid, (b) Phosphoric Acid.**

+  $\text{NH}_4\text{OH}$  until alkaline ( $\text{NH}_4$ )<sub>2</sub>S in slight excess. Warm and allow to settle. Filter and wash with water containing a little ( $\text{NH}_4$ )<sub>2</sub>S.

Precipitate: Treat + cold, dilute HCl (1—6).		Filtrate: Reserve for examination of Groups IV. and V.
Residue: NiS, CoS. Examine according to methods previously given.	Filtrate: Examine small portion, after boiling out $\text{H}_2\text{S}$ , for (a) oxalic acid by adding a slight excess of $\text{NH}_4\text{OH}$ and then acidifying with acetic acid + $\text{CaCl}_2$ , a white precipitate = $\text{CaC}_2\text{O}_4$ .	

If oxalic acid is found to be present, evaporate entire filtrate to dryness and ignite gently to decompose oxalates. Allow dish to become cold; dissolve in dilute HCl and proceed, using either of the previous schemes of analysis.

(b) Examine a small portion of filtrate according to 191. If phosphoric acid is found to be present, use the following scheme of analysis.

(Note.—If oxalic acid and phosphoric acid are both present, destroy the oxalic acid according to method given above and then analyze the solution according to the method following.)

Boil the filtrate with a few drops of  $\text{HNO}_3$ , and examine a small portion for Fe according to 79.

Add to remainder of filtrate  $\text{Fe}_2\text{Cl}_6$ , neutralize with  $\text{Na}_2\text{CO}_3$ , acidify slightly with acetic acid, add  $\text{NaC}_2\text{H}_3\text{O}_2$  and boil.

Precipitate: Examine for Al, Cr. Heat with excess of NaOH + NaClO. Filter and reject the precipitate. To filtrate, add $\text{NH}_4\text{Cl}$ , in excess, boil and filter.		Filtrate: Examine for Mn, Zn, Ba, Sr, Ca, Mg, according to methods used in the regular systematic grouping.
Precipitate: White, flocculent, shows presence of Al.	Filtrate: $\text{Na}_2\text{CrO}_4$ . Acidify with $\text{HC}_2\text{H}_3\text{O}_2$ and examine for Cr, according to 11.	

### Alternative Method for Use in Presence of Oxalates and Phosphates.

Treat the filtrate from Group II. with Sn and  $\text{HNO}_3$ . Evaporate to dryness and gently ignite. The oxalic acid will be decomposed and the phosphoric acid removed as phosphate of tin. Take up with dilute  $\text{HNO}_3$  and examine the filtrate according to the regular systematic grouping.

### Notes on Analysis of Group III.

I.—For action of  $(\text{NH}_4)_2\text{S}$  on the members of this group, compare Nos. 71, 76, 83, 88, 94, 99, 105, 110.

Tartaric acid, citric acid, and other organic matter, such as sugar, prevent the precipitation of hydroxides but not of sulphides, therefore Al and Cr are not precipitated by the group reagent in the presence of these matters.

If any of the above are found to be present, evaporate to dryness and destroy by ignition. Take up with dilute HCl and proceed with the regular scheme.

II.—If phosphates or oxalates be present, the fourth group will be precipitated on the addition of  $\text{NH}_4\text{OH}$ , and thus will be found with the third group. (See Nos. 116, 117, 121, 122, 126, 127.) Magnesium compounds are also similarly precipitated in the presence of phosphates. (See 131.)

In this case analyze the precipitate formed by the addition of third group reagents, according to the schemes given for use when phosphates or oxalates are present.

III.— $\text{BaCO}_3$  suspended in water precipitates, as hydroxides, salts derived from oxides of the type  $\text{R}_2\text{O}_3$ , (Fe, Al, Cr); but not salts derived from oxides of the type RO.

IV.—When compounds of this group are fused with a mixture of alkaline carbonate and nitrate, two of them give rise to combinations which dissolve in water, viz., Mn and Cr, which form respectively  $\text{Na}_2\text{MnO}_4$  and  $\text{Na}_2\text{CrO}_4$ . The former







dissolves in water, giving a purple solution of  $\text{Na}_2\text{Mn}_2\text{O}_8$ , with the simultaneous precipitation of  $\text{MnO}_2$ . The  $\text{Na}_2\text{CrO}_4$  dissolves in water giving a yellow solution. The other members of this group are converted by this treatment into oxides, insoluble in water.

V.—All of the members of this group give colored characteristic beads with the exception of Al and Zn. See Nos. 74, 92, 98, 104, 108.

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#### GROUP IV.

BARIUM. Ba.

Valence = II.

Use preferably  $\text{BaCl}_2$ .

113.  $(\text{NH}_4)_2\text{CO}_3$  or fixed alkaline carbonates precipitate  $\text{BaCO}_3$ .

White, pulverulent.

Insoluble in excess of reagents.

Insoluble in alkaline hydroxides.

Soluble in acids.

Soluble in solutions containing  $\text{CO}_2$ , with the formation of  $\text{Ba}(\text{HCO}_3)_2$ . This is decomposed by boiling or by the addition of soluble hydroxides with the re-precipitation of  $\text{BaCO}_3$ .

Slightly soluble in  $\text{NH}_4\text{Cl}$ .

114.  $\text{H}_2\text{SO}_4$  precipitates  $\text{BaSO}_4$ .

White, pulverulent.

Insoluble in acids (with the exception of concentrated  $\text{H}_2\text{SO}_4$ ).

115.  $\text{K}_2\text{CrO}_4$  precipitates  $\text{BaCrO}_4$ , distinction from Sr and Ca.

116.  $(\text{NH}_4)_2\text{C}_2\text{O}_4$  precipitates  $\text{BaC}_2\text{O}_4$ .

White, pulverulent.

Soluble in  $\text{HCl}$ ; solution hastened by warming.

Insoluble in  $\text{NH}_4\text{OH}$ .

117.  $\text{Na}_2\text{HPO}_4$  precipitates  $\text{BaHPO}_4$ .  
 White, flocculent.  
 Soluble in acids.  
 Insoluble in  $\text{NH}_4\text{OH}$ .
118. Ba compounds moistened with HCl on the loop of a clean platinum wire, impart to the flame a yellowish-green color.

STRONTIUM. Sr.                      Valence = II.

Use preferably  $\text{SrCl}_2$ .

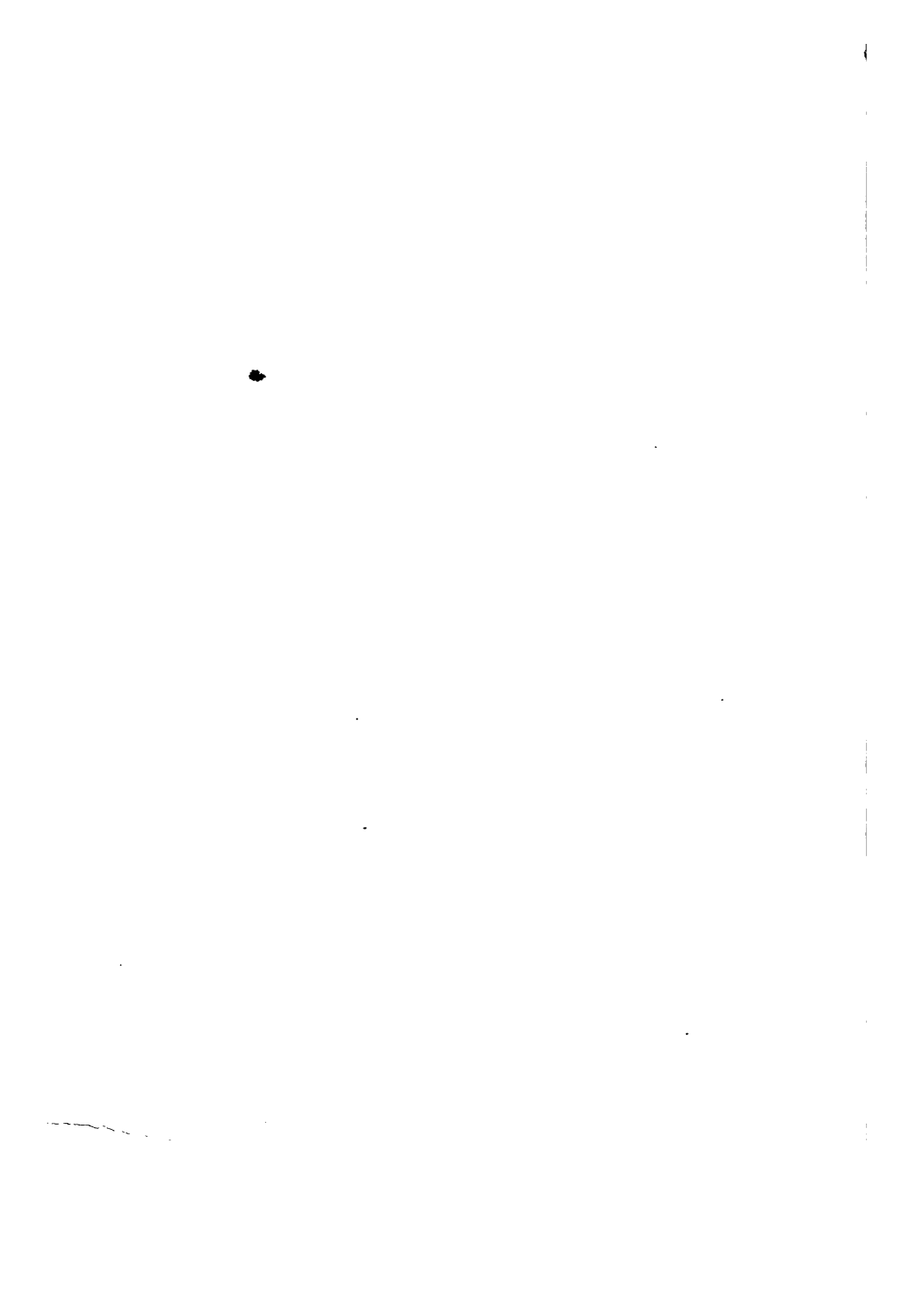
119.  $(\text{NH}_4)_2\text{CO}_3$  or fixed alkaline carbonates.  
 (Analogous to Ba. See 113.)
120.  $\text{H}_2\text{SO}_4$  precipitates  $\text{SrSO}_4$ .  
 White, pulverulent.  
 Very slightly soluble in water.  
 Strontium compounds are *immediately* precipitated by a solution of  $\text{CaSO}_4$ .
121.  $(\text{NH}_4)_2\text{C}_2\text{O}_4$  precipitates  $\text{SrC}_2\text{O}_4$ .  
 (Analogous to Ba. See 116.)
122.  $\text{Na}_2\text{HPO}_4$  precipitates  $\text{SrHPO}_4$ .  
 (Analogous to Ba. See 117.)
123.  $\text{Sr}(\text{NO}_3)_2$  is insoluble in alcohol.  
 (Distinction from calcium.)
124. Strontium compounds moistened with HCl, and heated on a Pt wire, impart a crimson color to the flame.

CALCIUM. Ca.                      Valence = II.

Use preferably  $\text{CaCl}_2$ .

125.  $(\text{NH}_4)_2\text{CO}_3$  or fixed alkaline carbonates precipitate  $\text{CaCO}_3$ .  
 (Analogous to Ba and Sr. See 113.)
126.  $(\text{NH}_4)_2\text{C}_2\text{O}_4$  precipitates  $\text{CaC}_2\text{O}_4$ .  
 (Analogous to Ba and Sr. See 116.)  
 Insoluble in acetic acid.





127.  $\text{Na}_2\text{HPO}_4$  precipitates  $\text{CaHPO}_4$ .  
(Analogous to Ba and Sr. See 117.)
128.  $\text{Ca}(\text{NO}_3)_2$  is soluble in alcohol. (Distinction from strontium.)
129.  $\text{H}_2\text{SO}_4$  precipitates  $\text{CaSO}_4$  only from concentrated solutions on addition of rather strong  $\text{H}_2\text{SO}_4$ .  
Decidedly soluble in water.
130. Calcium compounds moistened with  $\text{HCl}$ , and heated on a Pt wire, impart a brick-red color to the Bunsen flame.

### Analysis of Fourth Group.

+ HCl to slightly acid reaction.

Boil to separate sulphur.

Filter. Render alkaline with  $\text{NH}_4\text{OH}$ .

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Filtrate  $\text{BaCl}_2$ ,  $\text{SrCl}_2$ ,  $\text{CaCl}_2$  and Group V.

+  $(\text{NH}_4)_2\text{C}_2\text{O}_4$  and warm gently.

---

Precipitate  $\text{BaC}_2\text{O}_4$ ,  $\text{SrC}_2\text{O}_4$ ,  $\text{CaC}_2\text{O}_4$ .

Ignite in a porcelain dish.

Dissolve in  $\text{HC}_2\text{H}_3\text{O}_4$ .

Filtrate.

Examine for  
Group V.

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+  $\text{K}_2\text{CrO}_4$

---

Precipitate:  
 $\text{BaCrO}_4$ .  
See 115.

Filtrate  
 $\text{SrCrO}_4$ ,  $\text{CaCrO}_4$ .

---

+  $\text{NH}_4\text{OH}$  to alkaline reaction.  
+  $(\text{NH}_4)_2\text{C}_2\text{O}_4$ .

---

Precipitate  $\text{SrC}_2\text{O}_4$ ,  $\text{CaC}_2\text{O}_4$ .  
Dissolve in dilute  $\text{HNO}_3$ .

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Evaporate to dryness on steam-bath.

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Digest +  $\text{C}_2\text{H}_5\text{OH}$  absolute.

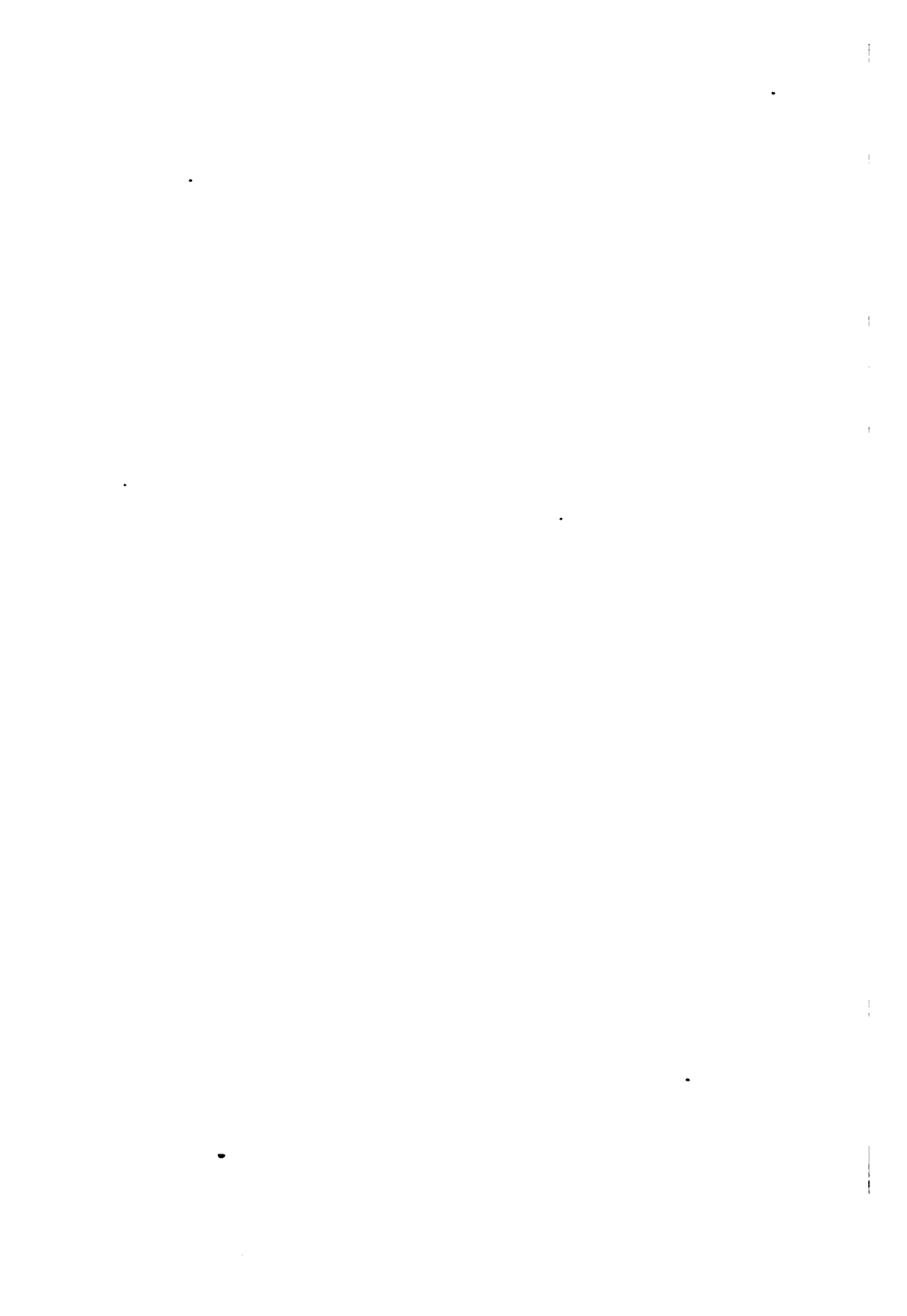
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Residue:  
 $\text{Sr}(\text{NO}_3)_2$ .  
Confirm by 120 or  
124.

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Filtrate:  
 $\text{Ca}(\text{NO}_3)_2$ ,  $\text{H}_2\text{O}$ . ater.  
Confirm by 126 or  
130.







**Notes.**

I.—In the scheme of analysis given for the fourth group,  $(\text{NH}_4)_2\text{C}_2\text{O}_4$  is used in preference to  $(\text{NH}_4)_2\text{CO}_3$ , chiefly on account of the greater insolubility of the oxalates.

II.—The fact of the different solubilities of the chlorides and nitrates of the members of this group in absolute alcohol is conveniently taken advantage of in methods of analysis of this group. Thus:—

$\text{BaCl}_2$ , insoluble in alcohol.

$\text{SrCl}_2$  } soluble in alcohol.  
 $\text{CaCl}_2$  }

$\text{Sr}(\text{NO}_3)_2$ , insoluble in alcohol.

$\text{Ca}(\text{NO}_3)_2$ , soluble in alcohol.

III.—The colors imparted to the Bunsen flame are characteristic and are specially important as confirmatory tests. (See Nos. 118, 124, 130.)

**GROUP V.**

**MAGNESIUM. Mg. Valence = II.**

Use preferably  $\text{MgSO}_4$ .

131.  $\text{Na}_2\text{HPO}_4$  in the presence  $\text{NH}_4\text{OH}$  and  $\text{NH}_4\text{Cl}$  precipitates  $\text{MgNH}_4\text{PO}_4$ . White, crystalline. Converted by heat into  $\text{Mg}_3\text{P}_2\text{O}_7$ .
132. Alkaline carbonates, oxalates or hydroxides fail to precipitate Mg solutions in the presence of salts of ammonium.
133. Solutions of Mg compounds containing an excess of  $(\text{NH}_4)_2\text{C}_2\text{O}_4$ , leave on evaporation to dryness and ignition of the residue, white  $\text{MgO}$ , practically insoluble in water.
134. Compounds of magnesium ignited with  $\text{Co}(\text{NO}_3)_2$  on charcoal yield a rose pink infusible mass.

POTASSIUM. K. Valence = I.

Use preferably KCl.

135.  $\text{PtCl}_4$  precipitates  $\text{K}_2\text{PtCl}_6$ . Yellow, heavy.  
 Insoluble in alcohol. (Distinction from Na.) Slightly soluble in cold water. Readily soluble in hot water, from which solution it crystallizes in yellow octahedra. (Similar compound with similar properties formed with  $\text{NH}_4\text{Cl}$ .)
136. Potassium compounds moistened with HCl give, when heated in the Bunsen flame on a Pt wire, a lilac coloration.

SODIUM. Na. Valence = I.

Use preferably NaCl.

137.  $\text{PtCl}_4$  forms  $\text{Na}_2\text{PtCl}_6$ , which, on evaporation, crystallizes in needle-shaped prisms.  
 Aurora-red.  
 Readily soluble in water and in alcohol.  
 (Distinction from K. See 135.)
138. Sodium compounds moistened with HCl, and heated on a Pt wire in the Bunsen flame, impart a strong daffodil yellow color.

AMMONIUM.  $\text{NH}_4$ . Valence = I.

Use preferably  $\text{NH}_4\text{Cl}$ .

139.  $\text{PtCl}_4$  forms  $(\text{NH}_4)_2\text{PtCl}_6$  similar to K compound.
140. All  $\text{NH}_4$  salts on being boiled + excess KOH or NaOH, yield  $\text{NH}_3$  gas, recognized by its characteristic odor, turning red litmus blue, or paper moistened with  $\text{CuSO}_4$  deep blue, or with mercurous nitrate black. With HCl, white fumes of  $\text{NH}_4\text{Cl}$  are formed.





### Analysis of Group V.

+  $(\text{NH}_4)_2\text{C}_2\text{O}_4$  in excess.

Evaporate to dryness. Ignite to expel ammonium salts.

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Extract with water.

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Residue: MgO. Confirm by 134, or dissolve in HCl. Add $\text{NH}_4\text{OH}$ and confirm by 131.	Filtrate $\text{Na}_2\text{CO}_3$ , $\text{K}_2\text{CO}_3$ . + HCl to acid reaction. Evaporate to dryness on water-bath + $\text{PtCl}_4$ . Add $\text{C}_2\text{H}_5\text{OH}$ to residue.	
	Precipitate $\text{K}_2\text{PtCl}_6$ . See No. 135.	Filtrate $\text{Na}_2\text{PtCl}_6$ . Evaporate sponta- neously. See 137.

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*Note.*—Examine for ammonium compounds in the original solution. (See 140.)

**Notes.**

I.—Dry oxalates decompose on ignition with the evolution of CO and the production of carbonates. In most cases these carbonates are decomposed with the evolution of CO<sub>2</sub> and production of oxides. (See analyses given for Group V. Also compare analysis of Groups III., IV., V., in presence of oxalates.)

II.—NH<sub>4</sub>Cl must be removed by ignition before testing for K and Na, as it forms a similar compound with PtCl<sub>4</sub>.

III.—All ammonium salts are volatile on ignition.

IV.—Nessler's solution (HgI<sub>2</sub>.2 KI + excess KOH) produces a brown precipitate of NH<sub>4</sub>g<sub>2</sub>I with ammonium compounds.

An extremely delicate test. Traces of NH<sub>3</sub> give a yellow or brown coloration.

V.—The colors imparted to the Bunsen flame are characteristic and are of special importance as confirmatory tests. (See 136 and 138.)







## B.—Reactions of the Acids.

### ACETIC ACID. $\text{HC}_2\text{H}_3\text{O}_2$ .

Use preferably  $\text{NaC}_2\text{H}_3\text{O}_2$ .

141.  $\text{H}_2\text{SO}_4 + \text{C}_2\text{H}_5\text{OH}$  form, on gently warming, ethyl acetate,  $\text{C}_4\text{H}_8\text{O}_2$ , possessing a characteristic, fragrant odor.
142.  $\text{Fe}_2\text{Cl}_6$  forms  $\text{Fe}_2(\text{C}_2\text{H}_3\text{O}_2)_6$ , a deep red solution, which on boiling is converted into basic ferric acetate.  
(See 80.)
143.  $\text{AgNO}_3$ , in rather concentrated solutions, precipitates  $\text{AgC}_2\text{H}_3\text{O}_2$ .  
White, crystalline.  
Easily soluble in  $\text{HNO}_3$ .
144. Acetates yield on ignition either carbonates or oxides, without blackening.

### ARSENIC ACID. $\text{H}_3\text{AsO}_4$ .

Use preferably  $\text{Na}_3\text{AsO}_4$ .

145.  $\text{H}_2\text{S}$  in acid solutions first effects a reduction with separation of sulphur, and subsequently precipitates  $\text{As}_2\text{S}_3$ .  
(See 45.)
146.  $\text{MgSO}_4$  in presence of  $\text{NH}_4\text{OH}$  and  $\text{NH}_4\text{Cl}$  precipitates  $\text{MgNH}_4\text{AsO}_4$ .  
(See 47.)  
(Distinction from arsenious acid.)  
This precipitate ignited forms  $\text{Mg}_2\text{As}_2\text{O}_7$ . Heated on charcoal it is decomposed with the production of a characteristic garlic-like odor.
147.  $\text{AgNO}_3$  precipitates  $\text{Ag}_3\text{AsO}_4$ .  
Reddish brown.  
Easily soluble in  $\text{HNO}_3$ .

Easily soluble in  $\text{NH}_4\text{OH}$ .

Slightly soluble in  $\text{NH}_4\text{NO}_3$ .

148. Arsenic acid is converted into arsenious acid by reducing agents, such as  $\text{H}_2\text{S}$ ,  $\text{SO}_2$ ,  $\text{FeSO}_4$ .  
For other reactions, see As, page 13.

#### ARSENIOUS ACID. $\text{H}_3\text{AsO}_3$ .

Use preferably  $\text{Na}_2\text{AsO}_3$ .

149.  $\text{H}_2\text{S}$  in acid solutions immediately precipitates  $\text{As}_2\text{S}_3$ .  
(Distinction from arsenic acid. See 39.)
150.  $\text{AgNO}_3$  precipitates  $\text{Ag}_3\text{AsO}_3$ .  
Yellow.  
Easily soluble in  $\text{HNO}_3$ .  
Easily soluble in  $\text{NH}_4\text{OH}$ .  
Slightly soluble in  $\text{NH}_4\text{NO}_3$ .
151. Oxidizing agents, such as  $\text{Fe}_2\text{Cl}_6$ ,  $\text{K}_2\text{Mn}_2\text{O}_8$ , or  $\text{K}_2\text{Cr}_2\text{O}_7$ , in acid solutions, also  $\text{Cl}$ ,  $\text{Br}$ ,  $\text{I}$  and  $\text{NaClO}$  in acid or alkaline solutions, convert arsenious acid into arsenic acid.  
For other reactions, see As, pages 12 and 13.

#### BORIC ACID. $\text{H}_3\text{BO}_3$ .

Use preferably  $\text{Na}_2\text{B}_4\text{O}_7$ .

152.  $\text{AgNO}_3$  in moderately concentrated solutions precipitates  $\text{AgBO}_2$ .  
White.  
Soluble in  $\text{HNO}_3$ .
153.  $\text{BaCl}_2$  in moderately concentrated solutions precipitates  $\text{Ba(BO}_2)_2$ .  
White.  
Soluble in  $\text{HCl}$  or  $\text{HNO}_3$ .
154. Turmeric paper moistened with solutions slightly acid with  $\text{HCl}$ , develops, on drying at a gentle heat, a fine rose-red color.





155. Solid borates moistened with concentrated  $\text{H}_2\text{SO}_4$  and mixed with a little glycerine or alcohol and set on fire, give a flame which is greenish on the edges.
156. A bead of a mixture of  $\text{KHSO}_4$  and  $\text{CaF}_2$  (4—1) dipped into a solid borate and then heated in a Bunsen flame, gives a greenish color which is instantly developed on the edges.

#### CARBONIC ACID. $\text{H}_2\text{CO}_3$ .

Use preferably  $\text{Na}_2\text{CO}_3$ .

157.  $\text{AgNO}_3$  precipitates  $\text{Ag}_2\text{CO}_3$ .  
White.  
Soluble in  $\text{HNO}_3$ .  
Soluble in  $\text{NH}_4\text{OH}$ .
158.  $\text{BaCl}_2$  precipitates  $\text{BaCO}_3$ .  
White, pulverulent.  
(See 113.)
159. Carbonates give with dilute acids an evolution of  $\text{CO}_2$  gas, which passed into  $\text{Ca}(\text{OH})_2$  gives a precipitate of  $\text{CaCO}_3$ .  
(See 125.)

#### CHROMIC ACID. $\text{H}_2\text{CrO}_4$ .

Use preferably  $\text{K}_2\text{CrO}_4$ .

160.  $\text{AgNO}_3$  precipitates dark red  $\text{Ag}_2\text{CrO}_4$ .
161.  $\text{BaCl}_2$  precipitates  $\text{BaCrO}_4$ . (See 115.)
162.  $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$  precipitates  $\text{PbCrO}_4$ .  
Yellow.  
Insoluble in dilute acids.  
Soluble in  $\text{KOH}$  or  $\text{NaOH}$ .
163. Reducing agents, such as  $\text{H}_2\text{S}$ ,  $\text{SO}_2$ ,  $\text{H}_3\text{AsO}_3$ , nascent hydrogen, in acid solutions, convert chromates (yellow or red) to chromium salts (green or violet).

HYDROBROMIC ACID.  $\text{HBr}$ .

Use preferably  $\text{NaBr}$ .

164.  $\text{AgNO}_3$  precipitates  $\text{AgBr}$ .

Pale yellow.

Insoluble in  $\text{HNO}_3$ .

Soluble with difficulty in  $\text{NH}_4\text{OH}$ .

165. Chlorine or chlorine oxides (acid solutions of hypochlorites or chlorates) liberate bromine which dissolves in  $\text{CS}_2$  or  $\text{CHCl}_3$ , coloring it a reddish brown.

166. Concentrated  $\text{H}_2\text{SO}_4$  decomposes solid bromides, giving reddish brown vapors of bromine.

Passed into dilute  $\text{NH}_4\text{OH}$  forms  $\text{NH}_4\text{Br}$ .

Colorless. (See 168.)

HYDROCHLORIC ACID.  $\text{HCl}$ .

Use preferably  $\text{NaCl}$ .

167.  $\text{AgNO}_3$  precipitates  $\text{AgCl}$ . (See 1.)

168. Solid chlorides mixed with solid  $\text{K}_2\text{Cr}_2\text{O}_7$  and covered with concentrated  $\text{H}_2\text{SO}_4$ , yield, on gently warming,  $\text{CrO}_2\text{Cl}_2$ .

Blood-red gas.

Passed into dilute  $\text{NH}_4\text{OH}$  forms  $(\text{NH}_4)_2\text{CrO}_4$ .

Yellow solution. (See 162.)

169. Concentrated  $\text{H}_2\text{SO}_4$  decomposes solid chlorides, giving off fumes of  $\text{HCl}$  gas.

HYDROCYANIC ACID.  $\text{HCN}$ .

Use preferably  $\text{KCN}$ .

170.  $\text{AgNO}_3$  precipitates  $\text{AgCN}$ . (See 4.)

171.  $\text{FeSO}_4$  and  $\text{Fe}_2\text{Cl}_6$  added to a solution of a cyanide, alkaline with  $\text{KOH}$  or  $\text{NaOH}$ , and then acidified with  $\text{HCl}$ , form  $\text{Fe}_4(\text{FeC}_6\text{N}_6)_3$ , "Prussian Blue."

172. Alkaline cyanides mixed with  $(\text{NH}_4)_2\text{S}$  and evaporated to dryness on the water-bath produce  $\text{NH}_4\text{CNS}$ . (See 79.)







173.  $\text{H}_2\text{SO}_4$  decomposes solid cyanides, giving off HCN gas.  
(Danger! *Highly poisonous!!*)

#### HYDROFLUORIC ACID. HF.

Use preferably  $\text{CaF}_2$ .

174. Solid fluorides mixed with concentrated  $\text{H}_2\text{SO}_4$  in a lead dish yield, on gently warming, HF, hydrofluoric acid gas, which etches glass.
175. (See 156.)

#### HYDRIODIC ACID. HI.

Use preferably NaI.

176.  $\text{AgNO}_3$  precipitates AgI.  
Straw yellow.  
Insoluble in  $\text{HNO}_3$ .  
Very slightly soluble in  $\text{NH}_4\text{OH}$ .
177. Chlorine or chlorine oxides (see 165) liberate iodine which dissolves in  $\text{CS}_2$  or  $\text{CHCl}_3$ , coloring it violet or purple. The color is destroyed by excess of Cl,  $\text{ICl}_3$  being formed. These decompositions take place before the similar reactions with bromides.
178. Starch made into a thin paste with water, boiled and then cooled, is colored an intense indigo blue by free iodine.
179. Concentrated  $\text{H}_2\text{SO}_4$  decomposes solid iodides, giving violet vapors of iodine, which soon condense as a dark colored solid.

#### HYDROSULPHURIC ACID. $\text{H}_2\text{S}$ .

Use preferably FeS.

180. Sulphides warmed with concentrated HCl give off  $\text{H}_2\text{S}$  gas.  
Characteristic odor.  
Papers moistened with  $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$  are blackened by the gas.

181. Solid sulphides fused +  $\text{Na}_2\text{CO}_3$  in a porcelain dish yield  $\text{Na}_2\text{S}$ . Fused mass placed on Ag and moistened gives black stain of  $\text{Ag}_2\text{S}$ .

#### NITRIC ACID. $\text{HNO}_3$ .

Use preferably  $\text{KNO}_3$ .

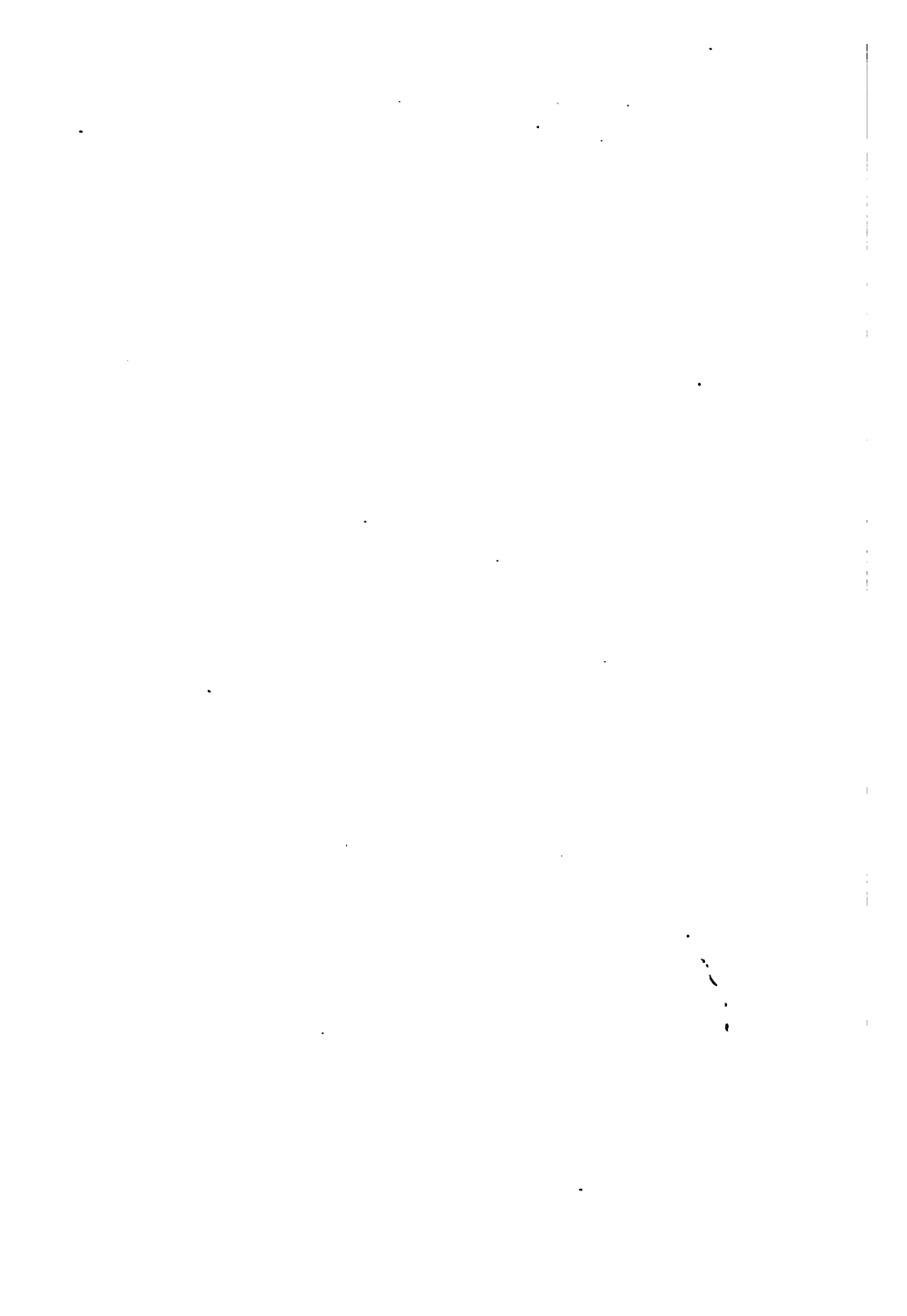
182. On adding a few drops of a solution of a nitrate to concentrated  $\text{H}_2\text{SO}_4$ , containing a clear crystal of  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ , a brown ring around the crystal is developed, due to the formation of  $\text{FeSO}_4(\text{NO})_2$ —an exceedingly unstable compound easily decomposed by heat, setting free  $\text{NO}$ , which on contact with the oxygen of the air forms brown fumes of  $\text{NO}_2$ .

#### OXALIC ACID. $\text{H}_2\text{C}_2\text{O}_4$ .

Use preferably  $(\text{NH}_4)_2\text{C}_2\text{O}_4$ .

183.  $\text{BaCl}_2$  precipitates  $\text{BaC}_2\text{O}_4$ .  
White, pulverulent.  
Easily soluble in  $\text{HCl}$  and  $\text{HNO}_3$ .
184.  $\text{AgNO}_3$  precipitates  $\text{Ag}_2\text{C}_2\text{O}_4$ .  
White.  
Easily soluble in  $\text{HNO}_3$ .  
Easily soluble in  $\text{NH}_4\text{OH}$ .
185.  $\text{CaCl}_2$  precipitates  $\text{CaC}_2\text{O}_4$ .  
Insoluble in  $\text{HC}_2\text{H}_3\text{O}_2$ .  
Insoluble in  $\text{NH}_4\text{OH}$ .  
Soluble in  $\text{HCl}$  and  $\text{HNO}_3$ .
186. Solid oxalates warmed with concentrated  $\text{H}_2\text{SO}_4$  are broken up, yielding  $\text{CO}_2$  and  $\text{CO}$  gases. If  $\text{MnO}_2$  is mixed with the powder,  $\text{CO}_2$  only is produced.
187. Oxalates and oxalic acid ignited decompose without separation of carbon.





PHOSPHORIC ACID.  $H_3PO_4$ .

Use preferably  $Na_2HPO_4$ .

188.  $BaCl_2$  precipitates  $BaHPO_4$ .  
 White, pulverulent.  
 Easily soluble in acids.
189.  $AgNO_3$  precipitates  $Ag_3PO_4$ .  
 Yellow.  
 Easily soluble in  $NH_4OH$  and in acids.
190. Mg salts in the presence of  $NH_4OH$  and  $NH_4Cl$  precipitate  $MgNH_4PO_4$ .  
 White, crystalline.  
 Insoluble in  $NH_4OH$ .  
 Soluble in acids.  
 Ignited, forms  $Mg_2P_2O_7$ , which, moistened with  $Co(NO_3)_2$ , and heated on charcoal, gives a blue mass. (Distinction from As. See 146.)
191.  $(NH_4)_2MoO_4$  in  $HNO_3$  solution precipitates, on warming,  $(NH_4)_3PO_4 \cdot 11MoO_3$ .  
 Yellow, pulverulent.  
 Insoluble in  $HNO_3$ .  
 Soluble in  $NH_4OH$  and in fixed alkalis.  
 $H_3AsO_4$  gives similar results.

SILICIC ACID.  $H_2SiO_3$ .

Use preferably  $Na_2SiO_3$ .

192.  $BaCl_2$  precipitates  $BaSiO_3$ .  
 White.
193.  $HCl$  decomposes moderately concentrated solutions, silicates forming  $H_2SiO_3$ .  
 White, gelatinous. On evaporation to dryness,  $SiO_2$  remains as a white insoluble powder. Heat on charcoal with  $Co(NO_3)_2$ ,  $SiO_2$ , or any silicate, gives a blue mass.

194. Silicates heated in a bead of microcosmic salt are decomposed with the separation of  $\text{SiO}_2$ , which floats about in the hot bead, unaffected.

SULPHURIC ACID.  $\text{H}_2\text{SO}_4$ .

Use preferably  $\text{Na}_2\text{SO}_4$ .

195.  $\text{BaCl}_2$  precipitates  $\text{BaSO}_4$ .  
(See 114.)

196. Sulphates fused with  $\text{Na}_2\text{CO}_3$  on charcoal are reduced to sulphides.

(See 181.)

The fused mass placed on silver coin and moistened with water, produces a black stain of  $\text{Ag}_2\text{S}$ .

TARTARIC ACID.  $\text{H}_2\text{C}_4\text{H}_4\text{O}_6$ .

Use preferably  $\text{Na}_2\text{C}_4\text{H}_4\text{O}_6$ .

197.  $\text{BaCl}_2$  precipitates  $\text{BaC}_4\text{H}_4\text{O}_6$ .  
White.  
Soluble in  $\text{HCl}$  and  $\text{HNO}_3$ .

198.  $\text{AgNO}_3$  precipitates from neutral tartrates  $\text{Ag}_2\text{C}_4\text{H}_4\text{O}_6$ .  
White.

Easily soluble in  $\text{HNO}_3$  and in  $\text{NH}_4\text{OH}$ .

The ammoniacal solution of this precipitate on being gently warmed forms on the side of the containing vessel an adherent brilliant coating of metallic silver.

If boiled, metallic silver is precipitated in the form of a black powder.

199.  $\text{KCl}$  precipitates white, crystalline  $\text{KHC}_4\text{H}_4\text{O}_6$ .

200.  $\text{H}_2\text{C}_4\text{H}_4\text{O}_6$ , or solid tartrates, yield on ignition a black residue and give off a characteristic odor of burnt sugar, accompanied by much intumescence.







## Analysis of the Acids.

### (a) ARSENIC ACID.

Boil a portion of the original solution with an excess of  $\text{Na}_2\text{CO}_3$ . To the filtrate add  $\text{NH}_4\text{OH}$ ,  $\text{NH}_4\text{Cl}$ ,  $\text{MgSO}_4$ . Test the precipitate formed for  $\text{MgNH}_4\text{AsO}_4$ . (See No. 146.) This precipitate may also contain  $\text{MgNH}_4\text{PO}_4$ .

### (b) ARSENIOS ACID.

Acidify the filtrate from the precipitate caused by the addition of  $\text{MgSO}_4$  with  $\text{HCl}$ , warm and pass  $\text{H}_2\text{S}$ ; a yellow precipitate is  $\text{As}_2\text{S}_3$ . Confirm by 149.

### (c) CHROMIC ACID.

To the filtrate from the  $\text{As}_2\text{S}_3$  in (b), add  $\text{NH}_4\text{OH}$  till alkaline. (See 163 and 89, 88, 92.)

### (d) CARBONIC ACID.

Add dilute  $\text{HCl}$  to a portion of the original solution and pass the gas evolved through a solution of  $\text{Ca(OH)}_2$ . (See 159.)

### (e) HYDROFLUORIC ACID.

Evaporate a portion of the original solution to dryness and examine the powder obtained by 174.

### (f) HYDROSULPHURIC ACID.

(See 180.)

### (g) NITRIC ACID.

To a portion of the original solution, add a slight excess of  $\text{Pb(C}_2\text{H}_3\text{O}_2)_2$ . Filter and remove the excess of  $\text{Pb}$  from the filtrate with dilute  $\text{H}_2\text{SO}_4$ . Concentrate the filtrate and examine according to 182.

### (h) ACETIC ACID.

To a portion of the original solution, add a slight excess of  $\text{Pb(NO}_3)_2$ . Filter and examine the filtrate by 141 or 142.





*Treat the remainder of the original solution in the following manner:—*

Dilute the solution, warm and saturate with  $H_2S$ . Reject the precipitate, and to the filtrate add an excess of  $Na_2CO_3$ . Boil and filter. Reject the precipitate as before, neutralize the filtrate with  $HNO_3$ , and examine the solution for the remaining acids as indicated below.

(i) BORIC ACID.

Examine a portion of the solution according to 154, or evaporate a portion to dryness and examine according to 155 or 156.

(j) HYDRIODIC ACID.—(k) HYDROBROMIC ACID.

Examine a portion of the solution according to 177 and 165.

(l) HYDROCHLORIC ACID.

Examine a portion of the solution according to 167, or, preferably,

Evaporate a portion of the solution and examine according to 168.

(m) HYDROCYANIC ACID.

To a portion of the solution add concentrated  $H_2SO_4$ , warm gently and pass the gas evolved into  $KOH$ . Examine this solution according to 171 or 172.

(n) OXALIC ACID.

Acidify a portion of the solution with acetic acid and add  $CaCl_2$ . (See 185.)

This precipitate on ignition forms  $CaCO_3$ , which effervesces with acid.

Evaporate a portion of the solution and examine according to 186.

(o) PHOSPHORIC ACID.

Examine a portion according to 190 or 191 (in absence of silicic acid).



*Treat the remainder of the original solution in the following manner:—*

Dilute the solution, warm and saturate with  $\text{H}_2\text{S}$ . Reject the precipitate, and to the filtrate add an excess of  $\text{Na}_2\text{CO}_3$ . Boil and filter. Reject the precipitate as before, neutralize the filtrate with  $\text{HNO}_3$ , and examine the solution for the remaining acids as indicated below.

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Examine a portion of the solution according to 154, or evaporate a portion to dryness and examine according to 155 or 156.

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Examine a portion of the solution according to 177 and 165.

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Examine a portion of the solution according to 167, or, preferably,

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This precipitate on ignition forms  $\text{CaCO}_3$ , which effervesces with acid.

Evaporate a portion of the solution and examine according to 186.

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Examine a portion according to 190 or 191 (in absence of silicic acid).



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Dilute the solution, warm and saturate with  $H_2S$ . Reject the precipitate, and to the filtrate add an excess of  $Na_2CO_3$ . Boil and filter. Reject the precipitate as before, neutralize the filtrate with  $HNO_3$ , and examine the solution for the remaining acids as indicated below.

(i) BORIC ACID.

Examine a portion of the solution according to 154, or evaporate a portion to dryness and examine according to 155 or 156.

(j) HYDRIODIC ACID.—(k) HYDROBROMIC ACID.

Examine a portion of the solution according to 177 and 165.

(l) HYDROCHLORIC ACID.

Examine a portion of the solution according to 167, or, preferably,

Evaporate a portion of the solution and examine according to 168.

(m) HYDROCYANIC ACID.

To a portion of the solution add concentrated  $H_2SO_4$ , warm gently and pass the gas evolved into  $KOH$ . Examine this solution according to 171 or 172.

(n) OXALIC ACID.

Acidify a portion of the solution with acetic acid and add  $CaCl_2$ . (See 185.)

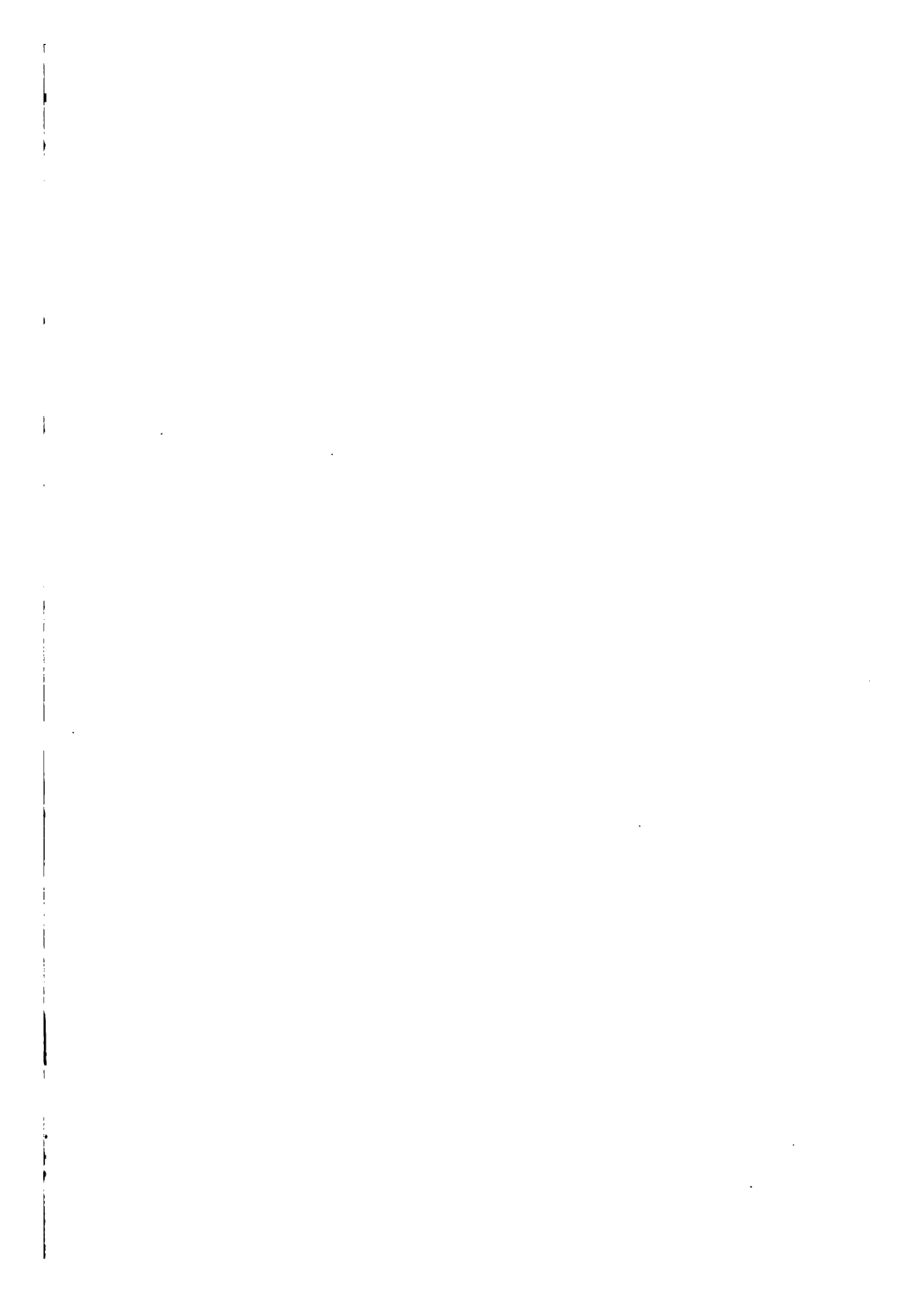
This precipitate on ignition forms  $CaCO_3$ , which effervesces with acid.

Evaporate a portion of the solution and examine according to 186.

(o) PHOSPHORIC ACID.

Examine a portion according to 190 or 191 (in absence of silicic acid).





*Treat the remainder of the original solution in the following manner:—*

Dilute the solution, warm and saturate with  $\text{H}_2\text{S}$ . Reject the precipitate, and to the filtrate add an excess of  $\text{Na}_2\text{CO}_3$ . Boil and filter. Reject the precipitate as before, neutralize the filtrate with  $\text{HNO}_3$ , and examine the solution for the remaining acids as indicated below.

(i) BORIC ACID.

Examine a portion of the solution according to 154, or evaporate a portion to dryness and examine according to 155 or 156.

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Examine a portion of the solution according to 177 and 165.

(l) HYDROCHLORIC ACID.

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Acidify a portion of the solution with acetic acid and add  $\text{CaCl}_2$ . (See 185.)

This precipitate on ignition forms  $\text{CaCO}_3$ , which effervesces with acid.

Evaporate a portion of the solution and examine according to 186.

(o) PHOSPHORIC ACID.

Examine a portion according to 190 or 191 (in absence of silicic acid).





## (p) SILICIC ACID.

Evaporate a portion of the solution to dryness and examine according to 194.

## (q) SULPHURIC ACID.

Examine a portion of the solution according to 195, or evaporate to dryness and examine according to 196.

## (r) TARTARIC ACID.

Evaporate a portion of the solution to dryness and examine according to 200.

### Notes on Analysis of the Acids.

I.  $\text{Na}_2\text{CO}_3$  is used to precipitate the bases before the examination for certain acids. Arsenic and arsenious compounds are not removed by this treatment. In the presence of organic acids or ammonium salts, certain metals, such as Cu, Hg, Fe, etc., are not removed by this treatment; hence the first treatment with  $\text{H}_2\text{S}$ , by means of which the above are removed as sulphides.

II. Chromic acid compounds are reduced by  $\text{H}_2\text{S}$  to chromium salts. The change in color from yellow or red of the chromate to green or purple of the chromium salt is characteristic, and the resultant solution answers to any of the regular tests for chromium salts.

III.  $\text{HCN}$  produces a turbidity in lime water similar to that produced by  $\text{CO}_2$ . (See Cl.) In case this acid is present, add *an excess* of  $\text{AgNO}_3$ , whereby both the  $\text{AgCN}$  and  $\text{Ag}_2\text{CO}_3$  are precipitated. Shake and allow precipitate to settle. Decant the clear liquid. On adding  $\text{HNO}_3$  dilute to the precipitate, the carbonate dissolves with effervescence, setting free  $\text{CO}_2$ . The cyanide is unaffected.

IV. Before testing for  $\text{HNO}_3$ , the addition of  $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$ , effects the removal of chromates, bromides, and iodides.

The first of these would be reduced by the  $\text{FeSO}_4 + \text{H}_2\text{SO}_4$  to a dark-colored solution, while the bromides and iodides would yield bromine and iodine, which would give misleading indications. Before examining for  $\text{HC}_2\text{H}_3\text{O}_2$ ,  $\text{Pb}(\text{NO}_3)_2$  is added to effect the removal of the same substances which also interfere with the examination for this acid. Chromic acid, bromine, and iodine, being oxidizing agents, prevent the formation of the ethyl acetate, and are therefore removed.

V. When a dry chloride mixed with dry  $\text{K}_2\text{Cr}_2\text{O}_7$  is moistened with concentrated  $\text{H}_2\text{SO}_4$ ,  $\text{CrO}_2\text{Cl}_2$ , a blood-red gas is given off. Bromides and iodides do not form analogous compounds. They are decomposed by concentrated  $\text{H}_2\text{SO}_4$ , setting free bromine and iodine respectively. These colored vapors might easily be mistaken for the gas  $\text{CrO}_2\text{Cl}_2$ , hence the subsequent treatment with ammonia, the formation of a chromate with its characteristic yellow color, and precipitations yielded by such metals as Pb. The bromine and iodine dissolve in the  $\text{NH}_4\text{OH}$  with the formation of colorless compounds.

VI. In examining for phosphoric acid with  $(\text{NH}_4)_2\text{HMoO}_4$ , silicic acid should be absent, as it forms a similar yellow precipitate. If silicic acid is present, it should be removed by 193.

VII. Tartaric acid is decomposed on ignition with blackening; acetic and oxalic acids decompose without blackening. Organic matter, such as dust accumulated from the air, or filter paper, decomposes with blackening, but without the characteristic odor of "burnt sugar."

VIII. All solid sulphides heated in air or oxygen yield  $\text{SO}_2$ .







## Solubility of the Metals in the Common Mineral Acids.

HCl, HNO<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub>.

1. HNO<sub>3</sub> is the general solvent for the metals. All the metals dissolve in this acid, with evolution of nitrogen oxides, with the exception of Sn and Sb, which form insoluble oxides, and Au and Pt, which are unaffected.

2. HCl is not so general a solvent for the metals.

Cd, As, Sn, Fe, Al, Cu, Mn, Zn and fourth and fifth group metals dissolve in HCl.

Ni and Co are slowly attacked.

Sb is dissolved with difficulty in concentrated HCl.

3. H<sub>2</sub>SO<sub>4</sub>, dilute, dissolves the same metals given above (excepting Sn), with the evolution of Hydrogen gas.

H<sub>2</sub>SO<sub>4</sub>, concentrated, hot, dissolves Ag, Cu, Bi, Hg and heavy metals generally with the evolution of SO<sub>2</sub> gas.

The metals easily dissolved by dilute H<sub>2</sub>SO<sub>4</sub> are, as a rule, unaffected by cold concentrated H<sub>2</sub>SO<sub>4</sub>. Boiled with concentrated H<sub>2</sub>SO<sub>4</sub>, they are dissolved with the evolution of SO<sub>2</sub> gas.

4. A mixture of concentrated HCl and concentrated HNO<sub>3</sub>, termed aqua regia, is the solvent for gold and platinum. They dissolve forming chlorides.

TABLE OF SOLUBILITIES.

	Acetate.	Arsenate.	Arsenite.	Borate.	Bromide.	Carbonate.	Chlorate.	Chloride.	Chromate.	Cyanide.	Fluoride.	Iodide.	Nitrate.	Oxalate.	Oxide.	Phosphate.	Silicate.	Sulphate.	Sulphide.	Tartrate.	Chloro- Platinates.
Ag	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..
Pb	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..
Hg. II.	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..
Hg. II.	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..
Bi	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..
Cu	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..
Cd	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..
Sn II.	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..
Sn IV.	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..
Sb	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..
Fe II.	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..
Fe IV.	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..
Al	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..
Cr	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..
Mn	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..
Zn	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..
Ni	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..
Co	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..
Ba	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..
Sr	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..
Ca	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..
Mg	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..
K.	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..
Na	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..
NH <sub>4</sub>	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..

a = soluble in water.  
 b = soluble in acids.  
 c = insoluble in acids.  
 ab = sparingly soluble in water.  
 bc = sparingly soluble in acids.

*Note.*—For more complete information on the solubilities, refer to the preliminary reactions given on the metals and on the acids.



1

2

### A. Treatment of a Solid (*not a Metal or Alloy*).

(a) Extract all substances soluble in boiling water.

Ascertain the reaction of this solution with litmus paper. Analyze a portion of the solution for the bases, in the usual manner.

According to the bases found to be present, examine the remainder of the solution for the acids which can be present. (See Table of Solubilities.)

(b) From the residue from (a), extract all substances soluble in HCl, dilute and concentrated, hot and cold.

Analyze a portion of this solution for the bases in the usual manner.

Ascertain what acids can be present (see Table of Solubilities) and examine the remainder of the solution for these.

(c) From the residue from (b), extract all substances soluble in HNO<sub>3</sub>, dilute and concentrated, hot and cold.

Analyze a portion of this solution for the bases in the usual manner.

Ascertain what acids can be present (see Table of Solubilities) and examine the remainder of the solution for these.

(d) From the residue from (c), extract all substances soluble in aqua regia (3 parts concentrated HCl, + 1 part concentrated HNO<sub>3</sub>). Proceed as before.

(e) From the residue from (d), extract all substances soluble in NH<sub>4</sub>OH. Examine for silver salts.

(f) From the residue from (e), extract all substances soluble in KOH or NaOH.

Examine for Pb or Sn compounds.

(g) Fuse residue from (f) + NaKCO<sub>3</sub> in iron crucible. Extract with water and examine solution for silicates and sulphate. Residue heat + HC<sub>2</sub>H<sub>3</sub>O<sub>2</sub>. Solution. Examine for Ba + Sr. Residue fuse + KHSO<sub>4</sub> on Pt. Dissolve in water and examine solution for Fe, Al, Cr.

### B. Treatment of a Solid (*a Metal or Alloy*).

Reduce the alloy to small fragments.

Place in a porcelain dish and warm + concentrated  $\text{HNO}_3$  (use not more than 1 gram of the alloy).

Repeat the treatment with acid, if necessary, until no metallic particles remain. Evaporate to dryness. Add water containing a little  $\text{HNO}_3$ , filter, wash.

Residue: Oxides of Sb and Sn heat + hot concentrated  $\text{H}_2\text{C}_2\text{H}_3\text{O}_6$ . Solution. Examine for Sb by 64. If residue remains, examine for Sn by fusing +  $\text{Na}_2\text{CO}_3$  + S, extracting  $\text{Na}_2\text{SnS}_3$  with water, and examining solution for Sn by 58.

Examine the  $\text{HNO}_3$  solution from the residue of Sb and Sn oxides for first, second, and third groups. (Fourth and fifth group metals are rarely found in alloys.)

NOTE (1).—If Au and Pt are present, they will be found with the residue of Sb and Sn oxides, as they are insoluble in  $\text{HNO}_3$ . Suspend the residue in a little water, add bromine water, and warm gently. When the Au and Pt are dissolved, filter. Examine the residue for Sb and Sn as before. Divide the filtrate into two portions. Boil out excess of bromine. Examine one portion for Au by precipitation with  $\text{FeSO}_4$  or oxalic acid. Examine the other portion for Pt by addition  $\text{KBr}$ . Evaporate and add alcohol. Precipitate =  $\text{K}_2\text{PtBr}_6$ .

NOTE (2).—If the alloy contains phosphorus, it will be found in the residue from the  $\text{HNO}_3$  treatment, combined as stannic phosphate. The fusion with the  $\text{Na}_2\text{CO}_3$  + S will give  $\text{Na}_2\text{SnS}_3$  and  $\text{Na}_3\text{PO}_4$ . On acidifying this with acid,  $\text{SnS}_2$  will be precipitated and the solution will contain  $\text{H}_3\text{PO}_4$ . Examine this solution for phosphoric acid. (See 191.)







## Questions in Qualitative Analysis.

1. A solution having an alkaline reaction is precipitated with dilute HCl. What may the precipitate contain? How would the ordinary course of analysis be modified?
2. What would be the effect of precipitating the metals with  $\text{H}_2\text{S}$ , without removal of the first group with HCl? Give a scheme for the separation of the precipitate obtained.
3.  $\text{AgI}$  and  $\text{Ag}_3\text{PO}_4$  are both yellow. How would you distinguish between them?  $\text{PbI}_2$  and  $\text{PbCrO}_4$ ?
4. A precipitate consisting of a mixture of  $\text{AgCl}$ ,  $\text{PbCl}_2$  and  $\text{Hg}_2\text{Cl}_2$  is exhausted with  $\text{NH}_4\text{OH}$ . The insoluble residue is treated with boiling  $\text{H}_2\text{O}$ , but no lead can be detected in the solution. Why?
5. Given a solution containing arsenious and arsenic compounds, how would you detect each? likewise in a solution containing stannous and stannic compounds, how would each be detected?
6. Explain the action of the following reducing agents: Nascent hydrogen, hydrogen gas + heat,  $\text{H}_2\text{S}$ ,  $\text{SO}_2$ , C, Fe. Give examples.
7. Explain the action of the following oxidizing agents, stating the conditions under which they are used:  $\text{HNO}_3$ , Cl, Br, I,  $\text{KNO}_3$ ,  $\text{KClO}_3$ ,  $\text{KClO}$ ,  $\text{K}_2\text{Mn}_2\text{O}_8$ ,  $\text{K}_2\text{Cr}_2\text{O}_7$ . Give examples.
8. Convert a stannous into a stannic salt, by the use of yellow ammonium sulphide, and explain the action.

9. Two yellow solutions which contain no  $\text{HNO}_3$  are treated with  $\text{H}_2\text{S}$ , sulphur separates in each case.  
(a) The solution becomes colorless.  
(b) The solution becomes green.  
What are your inferences? Proofs?
10. A solution has not been made acid with  $\text{HCl}$  before the precipitation by  $\text{H}_2\text{S}$ . At the moment of the introduction of the  $\text{H}_2\text{S}$ , a white precipitate appears. What may it be?
11. What would be the effect of an excessive amount of  $\text{HCl}$ ,  $\text{HNO}_3$ , or  $\text{H}_2\text{SO}_4$  before the addition of  $\text{H}_2\text{S}$ ? How could these undesirable conditions be rectified?
12. What would be the effect of allowing the precipitated sulphides of the second group to stand some time before analysis; of washing them with pure water?
13. A solution made by mixing aqueous solutions of the chlorides of the metals, contains a white precipitate. What may it be? Prove it.
14. A mixture of the sulphides of the second group is treated with concentrated  $\text{HNO}_3$ . An insoluble residue remains. What may it contain? Analyze it.
15. After  $\text{Pb}$  had been removed in the second group with  $\text{H}_2\text{SO}_4$ ,  $\text{NH}_4\text{OH}$  was added. The white flocculent precipitate obtained was dissolved in  $\text{HCl}$  and water added. No precipitate was obtained. Why?
16. In the separation of  $\text{As}_2\text{S}_3$ ,  $\text{Sb}_2\text{S}_3$ ,  $\text{SnS}_2$ , with concentrated  $\text{HCl}$ , why cannot a portion of the solution be examined directly for  $\text{Sn}$  by adding  $\text{HgCl}_2$  instead of using the method given?
17. Account for the occurrence of  $\text{Pb}$  in different parts of the scheme of analysis.





18. If Cd is not completely removed in the second group, where will it be found? Why? How can its presence be proved? Under what conditions is Cd not removed in the second group?
19. A solution containing Fe (ferric), Al, Cr, Mn, Zn, Ni, Co salts, is treated with  $\text{NH}_4\text{OH} + \text{NH}_4\text{Cl}$ . What is the precipitate obtained? Analyze it. Use KOH instead of  $\text{NH}_4\text{OH} + \text{NH}_4\text{Cl}$ . What is the result?  
If an insufficient quantity of  $\text{NH}_4\text{Cl}$  were added, what would be the result?  
  
What would be the effect if, after the addition of the  $\text{NH}_4\text{OH}$  and  $\text{NH}_4\text{Cl}$ , the whole were allowed to stand before analysis?
20. The third group precipitate is washed with pure water; what is the effect?
21. What would be the effect of allowing the precipitated sulphides of the third group to stand some time before analysis?
22. Which is preferable for the precipitation of the third group, colorless or yellow ammonium sulphide? Why?
23. In separating the precipitate containing the third group, with HCl, what would be the effect if the filtrate were not boiled to expel the  $\text{H}_2\text{S}$ ?
24. When the residue consisting of  $\text{Fe}_2(\text{OH})_6$  and  $\text{Mn}_2\text{O}_3(\text{OH})_2$  is dissolved in HCl, why is Cl given off, and why is it boiled out? What would be the effect if it were not boiled out?
25. What would be the result if a solution containing phosphates and oxalates were analyzed by the regular scheme of analysis instead of by the special scheme? Do these acids interfere with the analysis of the first and second groups?

26. Take a solution containing the members of the first, second and third groups. First add  $\text{NH}_4\text{OH}$  to alkaline reaction. Second, add it in excess. State the effect in each case. Use  $\text{KOH}$  similarly. What is the effect in each case?
27. Why is the precipitation of the fourth group with  $(\text{NH}_4)_2\text{C}_2\text{O}_4$  to be preferred to that by  $(\text{NH}_4)_2\text{CO}_3$ ?
28. Why must this precipitate be ignited before proceeding with the analysis?
29. What would be the effect of a solution of  $\text{CaSO}_4$  on a solution of  $\text{BaCl}_2$ ?  
 $\text{SrCl}_2$ ?  
 $\text{CaCl}_2$ ?
30. Given a solution containing  $\text{BaCl}_2$ ,  $\text{SrCl}_2$ ,  $\text{CaCl}_2$ . Analyze it with the use of  $\text{C}_2\text{H}_5\text{OH}$ .
31. Why is magnesium found in the fifth group and not in the fourth?
32. Why are  $\text{NH}_4$  compounds tested for in the original solution and not in the fifth group?
33. An acid solution containing ammonium salts was treated with  $\text{NaOH}$  and boiled, but no odor of  $\text{NH}_3$  was developed. Why?
34. What would be the effect of incomplete precipitation and incomplete washing of precipitates?
35. If the members of the various groups are incompletely precipitated by the group reagents, state where each member, so lost, will be found in the course of the regular scheme of analysis used.
36. What is the action of  $\text{HNO}_3$  on metals generally? What is the action of aqua regia? How do the products resulting from the action of  $\text{HNO}_3$  differ







from those resulting from the action of aqua regia?  
 Why does aqua regia dissolve Au and Pt while HCl or  $\text{HNO}_3$  does not?

37. Red oxide of lead is not dissolved by water nor  $\text{HNO}_3$ , but on the addition of a small quantity of solution of  $\text{KNO}_3$  or  $\text{H}_2\text{C}_2\text{O}_4$  to the  $\text{HNO}_3$  it is dissolved. Explain the action.
38.  $\text{Fe}_2\text{O}_3$ ,  $\text{Cr}_2\text{O}_3$ ,  $\text{Al}_2\text{O}_3$ , after ignition at a high heat, are practically insoluble in acids. Given the following fluxes:  
 $\text{Na}_2\text{CO}_3$ ,  $\text{KNO}_3$ ,  $\text{KHSO}_4$ ,  $\text{NaBO}_2$ ,  
 How could these oxides be brought into solution? State reasons.
39. Describe several ways of proving whether a powder under examination is an oxide.  
 State in what cases each method can be used. Give examples.
40. A powder given for analysis evolves oxygen on being heated. Does this fact necessarily demonstrate the presence of certain oxides? Draw up a list of the substances that yield oxygen on being heated.
41. On treating a powder with HCl and heating, Cl is evolved. Give a list of the substances which would cause this.
42. A dry substance is heated in a glass tube closed at one end.
  - (a) Liquid condenses in the cool part.
    1. It is neutral.
    2. It is alkaline.
    3. It is acid.
  - (b) Gases or fumes are given off.
    1. O is evolved.
    2.  $\text{CO}_2$  is evolved.
    3.  $\text{NO}_2$  is evolved.

(c) Sublimate is formed.

1. Hg.

2. S.

(d) Residue blackens.

State what substances are indicated by each result.

43. A powder submitted for analysis was:—

1. Heated on charcoal with  $\text{Na}_2\text{CO}_3$  in reducing and oxidizing flames.

2. Heated on charcoal with  $\text{Co}(\text{NO}_3)_2$ .

3. Borax and microcosmic salt beads were made with it.

4. HCl and Pt wire (flame test).

Give all deductions.

44. A solution containing no acetic acid, but a quantity of  $\text{K}_2\text{Cr}_2\text{O}_7$ , or some other oxidizing agent, gives, on testing for acetic acid by means  $\text{C}_2\text{H}_5\text{OH}$  and  $\text{H}_2\text{SO}_4$ , a peculiar odor. To what is it due?

45. In examining for  $\text{H}_3\text{AsO}_4$  by (a), analysis of the acids, why is the precipitate obtained still further tested for arsenic? Why is not the formation of this precipitate sufficient evidence?

46. Could a yellow precipitate formed in testing for  $\text{H}_3\text{AsO}_4$  in (b) be sulphur? Why not?

47. A solution containing Cu was tested for boric acid by 155. Was the test conclusive? Would you suggest a modification?

48. Under what conditions is it necessary to test a solution having an acid reaction for carbonates?

49. A solution was found to contain sulphides. It was subsequently tested for chromic acid. Was it found? State reasons.





50. Under what conditions does silver nitrate fail to precipitate Cl, Br, and I from compounds containing them?
51. How would you determine the presence of HCl, HBr, and HI in the cases of one, two, or all three of these acids being present? State reasons.
52. Given a solution containing free bromine and iodine, how could this solution be examined for HBr and HI?
53. Explain how the formation of Prussian blue in 171 is an evidence of HCN.
54. Is it rational to examine for HF, in solutions kept in glass vessels? Why?
55. Under what conditions may a solution contain sulphides? What would be the reaction of this solution toward litmus paper?  
What metals could be found in a solution containing sulphides?
56. How could a solution or a substance containing sulphides and sulphates be examined for each?
57. Is it necessary to examine a substance which is insoluble in water for the presence of nitrates?
58. Oxalates and carbonates when treated with concentrated  $\text{H}_2\text{SO}_4$  both yield  $\text{CO}_2$ . How can you distinguish between these acids by this test?
59. Under what conditions would you examine a neutral aqueous solution for phosphates?
60. An insoluble silicate is fused with  $\text{KHSO}_4$  and the fused mass is extracted with water. Where will the silica be found? Why?

61. A solution which is acid with  $\text{HCl}$ , is treated with  $\text{BaCl}_2$ . Is the white precipitate produced necessarily a sure indication of  $\text{H}_2\text{SO}_4$ ?
62. In what case may  $\text{BaSO}_4$  be found in a solution?
63. The residue left on the evaporation of a solution containing no carbonates, shows carbonates after ignition. To what may this be due?









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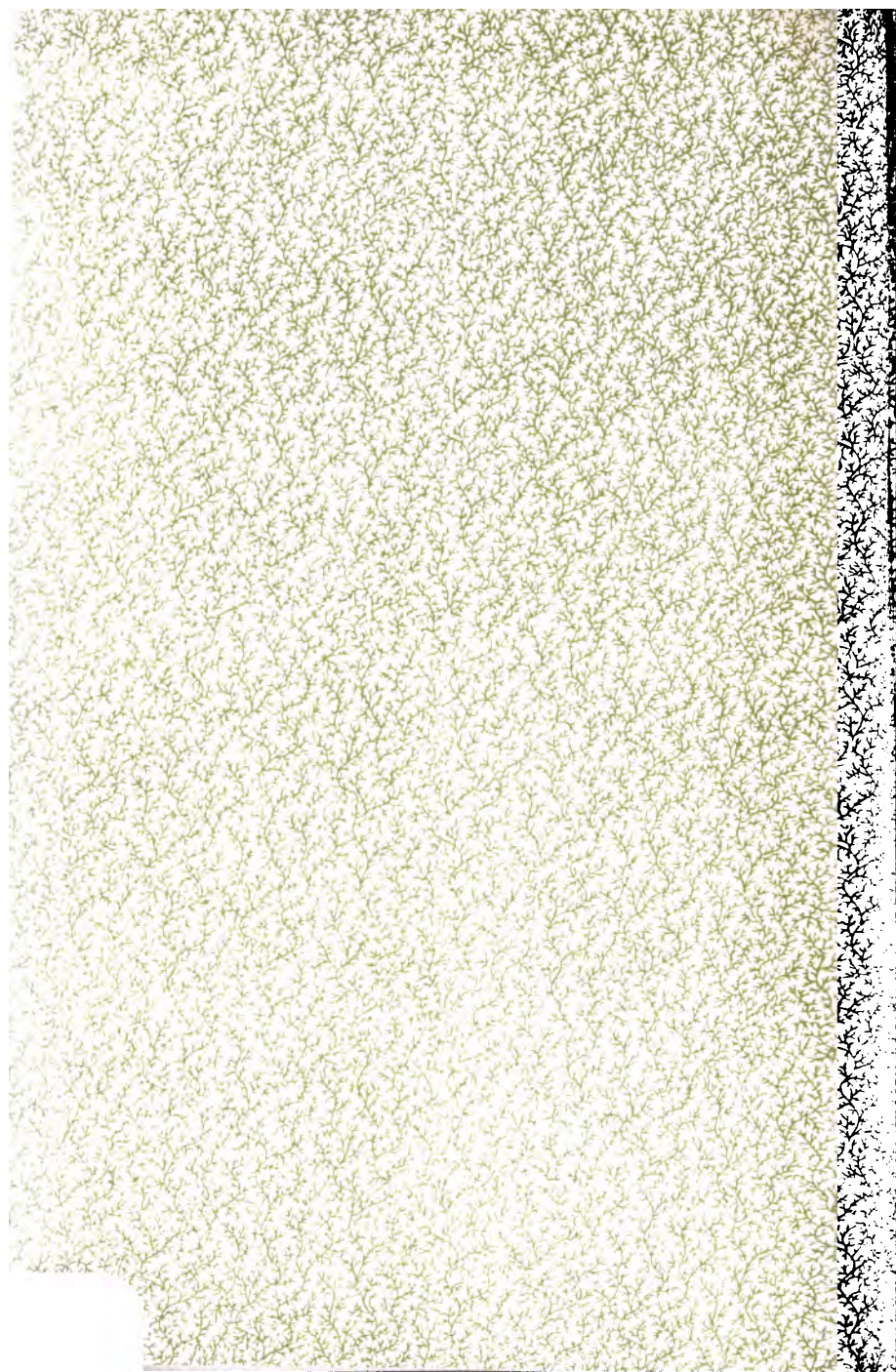


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